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THE SPECTRUM OF DOUBLY IONIZED MERCURY, Hg III¹

BY MARTIN W. JOHNS²

Abstract

The spectrum of mercury, excited in an electrodeless discharge, has been measured from 400 to 11,000 Å. From these data the analysis of Hg III has been extended to include 77 new terms of the configurations $5d^6s^2$, $5d^6s6p$, $5d^67s$, $5d^68s$, $5d^67p$, $5d^66d$, $5d^67d$, $5d^65f$, and seven unidentified even terms. Isotope shifts have been observed in 11 lines and confirm the classifications of these lines.

Introduction

In 1928 McLennan, McLay, and Crawford (7) classified about 40 of the most prominent ultra-violet lines of Hg III as transitions between the terms of the configurations $5d^6s$ and $5d^66p$. In 1935 Mack (6) reassigned J -values to two of their $5d^66p$ terms; replaced a third; and established the terms $5d^61^1_0$ and $5d^66p^9_0$. Recently Ricard (9) published a term scheme for the visible and near ultra-violet lines of Hg III, but did not identify any of the terms.

The present paper confirms the term scheme as established by McLennan, McLay, and Crawford and modified by Mack, with the exception of the term $5d^66p^9_0$, and extends the analysis to include 77 new terms of the configurations $5d^6s^2$, $5d^6s6p$, $5d^67s$, $5d^68s$, $5d^67p$, $5d^66d$, $5d^67d$, and $5d^65f$ and seven unidentified even terms. This analysis and Ricard's have not as yet been correlated, although the term scheme is confirmed by this investigation.

Experimental

The spectrum emitted by an electrodeless discharge (3) in mercury vapor was measured throughout the spectral region 11,000 to 400 Å. The infra-red and visible regions were photographed using Hilger E₁ quartz and glass prism spectrographs; the near ultra-violet with a 3-metre vacuum grating and an E₁ quartz spectrograph; and the region below 2000 Å with the 3-metre vacuum grating. The fainter lines around 2000 Å were also photographed with small quartz and fluorite spectrographs. Excitation characteristics (3) of the lines were studied in the entire region; these data made it possible to assign the lines fairly definitely to the various spectra, I, II, III, etc., of mercury.

In addition to the above-mentioned measurements, the wave-lengths of some 300 lines were measured relative to secondary international standards

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with a 21 ft. concave grating. These wave-lengths, estimated to be accurate to within 0.003 Å, provided internal standards for use with the prism spectrographs. Some of the lines on the grating plates showed hyperfine structures; when such lines were used as internal standards, these structures were taken into consideration in determining their mean wave-lengths. Internal standards for the vacuum region were obtained from the analysis of Hg II published by McLennan, McLay, and Crawford (8). The terms established by them were evaluated more accurately using the 21 ft. grating measurements. Classified ultra-violet lines, whose frequencies were determined from these term values, provided wave-length standards accurate to within 0.02 Å. In the region below 1000 Å these internal mercury standards were supplemented by Edlén's measurements (4) of the prominent lines of nitrogen, oxygen, and carbon present as impurities in the discharge. Edlén's wave-lengths were found to be in excellent agreement with the mercury standards below 1200 Å. A further check of the consistency of the standards was provided by the agreement of the wave-lengths measured in the first and second orders of the 3-metre vacuum grating.

TABLE I

Configuration	Term Symbol		Term value, cm. ⁻¹	Configuration	Term Symbol		Term value, cm. ⁻¹
	Even	Odd			Even	Odd	
5d ¹⁰		1 ₀	0.0*			18 ₀ ⁰	153254.6
5d _{5/2} ⁹ 6s		2 ₃	42850.0*			19 ₀ ⁰	154214.0
		3 ₃	46029.7*			20 ₀ ⁰	155797.0
5d _{3/2} ⁹ 6s		4 ₁	58405.5*			21 ₀ ⁰	156580.0
		5 ₂	61085.5*			22 ₀ ⁰	158205.0
5d _{5/2} ⁸ 5/2 6s ²		6 ₄	97894.0			23 ₀ ⁰	160790.5
5d _{5/2} ⁸ 6p _{1/2}		1 ₀ ⁰	103549.1*			24 ₀ ⁰	161282.2
		2 ₀ ⁰	105627.5*			25 ₀ ⁰	161432.0
5d _{5/2} ⁸ 5/2 6s ²		7 ₂	106028.2			26 ₀ ⁰	161462.0
5d _{3/2} ⁸ 3/2 6s ²		9 ₃	112227.1			27 ₀ ⁰	162155.0
		10 ₁	117055.1			28 ₀ ⁰	162972.2
5d _{5/2} ⁸ 6p _{3/2}		5 ₀ ⁰	117994.4*			29 ₀ ⁰	163452.7
		3 ₀ ⁰	118547.9*			30 ₀ ⁰	164905.6
5d _{5/2} ⁸ 6p _{1/2}		4 ₀ ⁰	118607.6*	5d ⁹ 6s6p		31 ₀ ⁰	165004.8
5d _{3/2} ⁸ 3/2 6s ²	11 ₃		118926.7			32 ₀ ⁰	166180.0
5d _{5/2} ⁸ 6p _{3/2}		6 ₀ ⁰	120928.1*			33 ₀ ⁰	166311.1
		7 ₀ ⁰	121601.9*			34 ₀ ⁰	167581.0
5d _{5/2} ⁸ 3/2 6s ²	12 ₄		122340.8			35 ₀ ⁰	169063.0
5d _{5/2} ⁸ 6p _{3/2}		8 ₀ ⁰	126556.6*			36 ₀ ⁰	169667.1
5d _{5/2} ⁸ 6p _{1/2}		9 ₀ ⁰	130702.1			37 ₀ ⁰	171366.6
5d _{3/2} ⁸ 3/2 6s ²	13 ₂		133731.2			38 ₀ ⁰	173970.0
		10 ₀ ⁰	134589.0*			39 ₀ ⁰	175512.5
5d _{5/2} ⁸ 6p _{3/2}		11 ₀ ⁰	134998.8*			40 ₀ ⁰	177281.5
		12 ₀ ⁰	136480.0*			41 ₀ ⁰	180247.4
		13 ₀ ⁰	149716.9			42 ₀ ⁰	183544.0
		14 ₀ ⁰	150276.0			43 ₀ ⁰	184698.7
		15 ₀ ⁰	150279.1			44 ₀ ⁰	187030.0
		16 ₀ ⁰	150857.5			45 ₀ ⁰	194904.7
		17 ₀ ⁰	151997.8			46 ₀ ⁰	196378.5

TABLE I—(Concluded)

Configuration	Term Symbol		Term value, cm. ⁻¹	Configuration	Term Symbol		Term value, cm. ⁻¹
	Even	Odd			Even	Odd	
$5d^9_{5/2} 7s$	15 ₃		178428.8	$5d^9_{3/2} 7p_{3/2}$		88 ₂ ^o	217670.4
	16 ₃		179038.9			89 ₁ ^o	217740.2
	17 ₁		182267.8			90 ₃ ^o	218006.5
	18 ₄		183923.2			91 ₀ ^o	218101.5
	19 ₂		184269.1	$5d^9_{5/2} 8s$	29 ₃		221681.4
$5d^9_{5/2} 6d$	20 ₅		184462.0		30 ₂		221913.2
	21 ₁		184798.6		31 ₃		224988.1
	22 ₃		185064.4	$5d^9_{5/2} 7d$	32 ₂ ^o		225489.3
	23 ₃		186124.2		33 ₂		225517.1
$5d^9_{3/2} 7s$	24 ₂		186221.8		34 ₃		225532.8
	25 ₄		186520.5	Unknown	35 ₂		226165.0
	26 ₀		189775.8		36 ₃		230369.0
	27 ₁		194078.7	$5d^9_{5/2} 5f$		92 ₁ ^o	230416.9
	28 ₂		194475.9	Unknown	37 ₃		231588.7
$5d^9_{5/2} 7p$		80 ₂ ^o	201800.6	$5d^9_{5/2} 5f$		93 ₂ ^o	231675.5
		81 ₃ ^o	201870.7			94 ₂ ^o	232102.7
		82 ₂ ^o	201883.5			95 ₄ ^o	232234.0
		83 ₂ ^o	202090.5	Unknown	38 ₄		235017.0
		84 ₂ ^o	202357.0		39 ₁		236279.2
$5d^9_{3/2} 7p_{1/2}$		85 ₃ ^o	202721.1		40 ₃		239710.5
		86 ₂ ^o	212421.9		41 ₁		245631.3
		87 ₁ ^o	213660.4	$5d^9 \ ^3D_{5/2}$ of Hg IV (approx.) 276000 cm. ⁻¹ .			

The ordinal numbers 8 and 14 have been reserved for the two unestablished $J=0$ terms of $5d^*6s^*$.

The ordinal numbers 47^o to 79^o have been reserved for unknown terms of $5d^*6s6p$.

*Established prior to this investigation.

The multiplet terms of Hg III are listed in Table I. The value zero is assigned to the normal state $5d^{10}1_0$; the other term values are relative to this datum. Term values marked with an asterisk were established prior to this investigation. Each term is assigned an ordinal number with its J -value indicated by a subscript. All the terms, except the seven even terms 35₂ to 41₁ inclusive, have been uniquely assigned to the electron configurations which are listed in Column 1. The nomenclature for jj coupling has been used in describing all the configurations.

The classified wave-lengths, together with visual estimates of their intensities, their frequencies, and term combinations, are given in Table II. Wave-lengths measured on the 21 ft. grating are given to within 0.001 Å, others to within 0.01 Å. A measure of the accuracy of the measurements is given by the difference " $\nu_{\text{observed}} - \nu_{\text{calculated}}$ " which is tabulated in Column 4.

The unique assignment of the terms to electron configurations is feasible in this spectrum because there is no appreciable overlapping of the terms arising from different configurations of the same parity, and hence no prominent inter-configuration perturbations. If large inter-configuration perturbations were present, terms with the same J -values arising from the perturbing configurations would share their properties, and it then would be meaningless to assign such terms to a single configuration. The distribution

TABLE II

Int.	λ (I.A.)	ν , cm. ⁻¹	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	Classification	Int.	λ (I.A.)	ν , cm. ⁻¹	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	Classification
1	8451.1	11829.6	— .7	$87_1^0 - 32_2$	4	5372.31	18608.8	.0	$88_2^0 - 39_1$
1	8243.7	12127.1	— 2.2	$7_3^0 - 13_2$ a	5	5272.73	18960.2	— .1	$85_3^0 - 29_2$
20d	8159.5	12252.3	4.1	$12_4 - 10_2^0$ a	30	5210.90	19185.2	.7	$28_2 - 87_1^0$
3d	8084.4	12366.1	3.6	$90_3^0 - 36_2$ a	2	5209.07	19192.0	— .1	$85_3^0 - 30_2$
20	7984.2	12521.3	1.6	$7_2 - 3_2^0$	9	5146.30	19426.0	1.1	$10_1 - 12_2^0$
15	7915.4	12630.1	1.3	$89_3^0 - 36_2$ b	1	5120.77	19522.9	— .5	$13_2 - 18_2^0$
7dd	7808.9	12802.3	— .8	$6_2^0 - 13_2$	2dd	5118.25	19532.5	— .3	$17_1 - 80_1^0$
3	7623.6	13113.5	2.6	$86_2^0 - 34_2$	7	5105.34	19581.9	.2	$27_1 - 87_1^0$
4d	7517.5	13298.6	— .6	$2_3^0 - 11_2$	1	5102.26	19593.7	2.8	$83_2^0 - 29_2$
3d	7401.7	13506.7	.7	$1_2^0 - 10_1$	2	5096.49	19615.9	.2	$17_1 - 82_2^0$
6d	7325.6	13647.0	.0	$10_1 - 9_2^0$	1	5049.53	19798.3	.4	$82_2^0 - 29_2$
20	6709.20	14900.8	.9	$7_2 - 6_2^0$	4	5046.37	19810.7	.0	$81_2^0 - 29_2$
8	6610.05	15124.3	.7	$4_1^0 - 13_2$	5	5043.27	19822.9	.1	$17_1 - 83_2^0$
20d	6584.02	15184.1	.8	$3_2^0 - 13_2$.2	$83_2^0 - 30_2$
30	6512.61	15350.6	.4	$25_4 - 81_2^0$	12	4991.15	20029.9	.2	$82_2^0 - 30_2$
50	6501.26	15377.4	— .2	$1_2^0 - 11_2$ c (5)	8	4987.96	20042.7	.2	$81_2^0 - 30_2$
40	6418.82	15574.9	1.2	$7_2 - 7_2^0$	90	4973.49	20101.0	.5	$6_4 - 5_2^0$ c
3	6388.22	15649.5	— .6	$24_2 - 81_2^0$	12	4869.85	20528.8	.4	$7_2 - 8_2^0$
40	6383.16	15661.9	— .4	$11_2 - 10_2^0$	15	4489.67	22267.1	.1	$85_2^0 - 31_2$
			.3	$24_2 - 82_2^0$	30	4470.56	22362.3	.5	$9_2 - 10_2^0$ c
15	6348.78	15746.7	.2	$23_2 - 81_2^0$	2	4420.22	22617.0	— 1.8	$87_1^0 - 39_1$
40	6343.71	15759.3	.0	$23_2 - 82_2^0$	3d	4417.01	22633.4	2.3	$84_2^0 - 31_2$
20	6299.93	15868.8	— .2	$24_2 - 83_2^0$	20	4392.120	22761.67	.0	$16_2 - 80_2^0$
35	6220.24	16072.1	.0	$11_2 - 11_2^0$	2	4390.88	22768.1	— .1	$85_2^0 - 32_2$
30	6170.95	16200.5	— .1	$25_4 - 85_2^0$	15	4385.489	22796.09	.1	$85_2^0 - 33_2$
10	6158.29	16233.8	1.0	$23_2 - 84_2^0$	8d	4382.53	22811.5	— .2	$85_2^0 - 34_2$
2d	6059.12	16499.5	.2	$24_2 - 85_2^0$	25	4378.638	22831.76	.0	$16_2 - 81_2^0$
2d	6041.25	16548.3	.4	$13_2 - 15_2^0$ d	40	4376.186	22844.55	.0	$16_2 - 82_2^0$
10	6023.56	16596.9	.0	$23_2 - 85_2^0$	3d	4375.37	22848.8	.0	$13_2 - 21_2^0$
3	5981.28	16714.2	.7	$2_2^0 - 12_4$	30	4336.881	23051.59	.0	$16_2 - 83_2^0$
5d	5948.33	16806.8	.5	$22_2 - 81_2^0$	6	4326.933	23104.58	.0	$82_2^0 - 31_2$
2	5943.99	16819.1	.0	$22_2 - 82_2^0$	5	4324.57	23117.2	— .2	$81_2^0 - 31_2$
15	5879.83	17002.6	.6	$21_2 - 80_2^0$	5	4313.920	23174.28	— 1.6	$84_2^0 - 34_2$ a
1	5876.16	17013.2	2.7	$90_3^0 - 38_4$	1	4310.16	23194.5	— 1.0	$28_2 - 88_2^0$
10d	5851.61	17084.6	— .3	$21_2 - 82_2^0$	5	4297.25	23264.2	— .1	$28_2 - 89_2^0$
2	5837.80	17125.0	— 1.3	$13_2 - 16_2^0$	3	4267.28	23427.6	.8	$83_2^0 - 33_2$ e
6	5781.12	17292.9	.3	$22_2 - 84_2^0$	35	4264.674	23441.88	.0	$15_2 - 81_2^0$
			1.0	$21_2 - 83_2^0$	1	4264.27	23444.1	.2	$85_2^0 - 35_2$
2	5695.68	17552.3	— 1.0	$11_2 - 12_2^0$	8	4262.346	23454.68	.0	$15_2 - 82_2^0$
10	5679.47	17602.4	.6	$19_2 - 81_2^0$	1	4248.58	23530.7	1.3	$28_2 - 90_2^0$
15	5661.99	17656.7	.0	$22_2 - 85_2^0$	15	4237.424	23592.62	.9	$27_1 - 88_2^0$
10	5571.06	17944.9	— 1.1	$28_2 - 86_2^0$	3	4234.79	23607.3	1.5	$82_2^0 - 32_2$
			1.2	$10_1 - 11_2^0$	5	4232.735	23618.76	.1	$81_2^0 - 32_2$
			.5	$18_4 - 81_2^0$	25	4230.086	23633.55	.0	$82_2^0 - 33_2$
5d	5570.11	17948.0	.9	$86_2^0 - 36_2$	10	4227.800	23646.33	— .1	$81_2^0 - 33_2$
1	5500.36	18175.6	2.1	$91_2^0 - 39_1$	20	4227.243	23649.44	.1	$82_2^0 - 34_2$
5	5473.18	18265.9	— .7	$13_2 - 17_2^0$.1	$81_2^0 - 34_2$
30	5450.210	18342.83	— .4	$27_1 - 86_2^0$	3	4224.96	23662.2	.5	$15_2 - 83_2^0$
5	5418.09	18451.6	— .4	$19_2 - 85_2^0$.7	$27_1 - 89_2^0$
1	5392.77	18538.2	— .8	$89_2^0 - 39_1$	15	4221.412	23682.11	— .1	$16_2 - 85_2^0$

TABLE II—(Continued)

Int.	λ (Å.)	ν , cm. ⁻¹	$\nu_{obs.} - \nu_{calc.}$	Classification	Int.	λ (Å.)	ν , cm. ⁻¹	$\nu_{obs.} - \nu_{calc.}$	Classification
80	4216.74	23708.4	.5	$6_4 - 7_3^0 c$	2	3016.06	33146.2	— .1	$81_3^0 - 38_4$
1	4198.63	23810.6	2.6	$84_4^0 - 35_2$	1	3001.84	33303.2	.6	$21_1 - 91_0^0$
6	4185.493	23885.34	.7	$26_0 - 87_1^0$	3	2994.49	33385.0	2.0	$16_2 - 86_2^0 d$
30	4177.994	23928.21	.0	$15_3 - 84_2^0$	2	2993.01	33401.5	.2	$19_2 - 88_2^0$
7	4161.586	24022.55	.0	$27_1 - 91_0^0$	1	2988.06	33456.8	.6	$12_4 - 20_3^0$
1	4152.42	24075.6	1.1	$83_2^0 - 35_2$	1	2986.57	33473.5	2.4	$19_2 - 89_1^0$
40	4122.10	24252.7	— .2	$9_3 - 12_2^0 c$	1	2963.21	33737.4	.0	$19_2 - 90_2^0$
3	4117.24	24281.3	— .2	$82_2^0 - 35_2$	6	2957.36	33804.1	1.7	$10_1 - 16_1^0$
25	4115.373	24292.30	.0	$15_3 - 85_2^0$	2	2933.17	34082.9	— .4	$18_4 - 90_2^0$
1	4115.07	24294.1	— .2	$81_3^0 - 35_2$	1	2912.21	34328.2	.3	$11_2 - 18_2^0$
15	3651.731	27376.50	.4	$12_4 - 13_3^0$	1	2829.51	35331.4	.4	$13_2 - 35_1^0 d$
1	3643.44	27438.8	.2	$24_2 - 87_1^0$	1	2823.71	35404.0	1.0	$17_1 - 88_2^0$
1	3619.03	27623.9	.6	$21_1 - 86_2^0$	1	2818.07	35474.9	2.5	$17_1 - 89_1^0$
7	3615.849	27648.17	.3	$85_2^0 - 36_3$	6	2781.92	35935.8	— .1	$13_2 - 36_2^0$
6	3609.07	27700.1	— .7	$13_2 - 25_2^0$	20	2724.39	36694.6	— .4	$6_4 - 10_2^0 c$
20	3578.738	27934.86	— .4	$12_4 - 14_2^0$	1d	2702.71	36989.0	— .4	$85_2^0 - 40_3$
1	3568.85	28012.3	.3	$84_2^0 - 36_3$	1	2676.28	37354.2	.6	$84_4^0 - 40_3$
6	3557.24	28103.7	.0	$2_3^0 - 13_2 c$	1	2666.78	37487.3	— 2.5	$9_3 - 13_3^0$
1	3551.09	28152.4	— .4	$19_2 - 86_2^0$	1	2657.41	37619.4	— .3	$83_2^0 - 40_3$
2	3535.39	28277.4	— 1.1	$83_2^0 - 36_3$	1	2656.29	37635.3	— .1	$13_2 - 37_2^0$
1	3509.29	28487.7	2.2	$82_2^0 - 36_3$	2d	2642.72	37828.5	1.5	$82_2^0 - 40_3$
5	3507.97	28498.4	.1	$81_3^0 - 36_3$	1	2641.93	37839.9	.1	$81_3^0 - 40_3$
4d	3500.34	28560.5	— .3	$7_2 - 10_2^0 c$	2	2627.36	38049.7	.8	$9_3 - 14_2^0$
1	3499.33	28568.8	.4	$80_2^0 - 36_3 f$	2	2587.76	38631.9	.4	$16_2 - 88_2^0$
2	3464.00	28860.1	— 1.7	$21_1 - 87_1^0$	3	2567.19	38941.4	.0	$12_4 - 24_2^0$
30	3462.936	28869.0	1.4	$85_2^0 - 37_3 a$	1	2566.08	38958.3	.7	$16_2 - 90_2^0$
8d	3450.76	28970.8	.2	$7_2 - 11_1^0 c$	1	2547.45	39243.2	1.6	$15_3 - 88_2^0$
30	3419.983	29231.56	— .2	$84_2^0 - 37_3$	5	2545.16	39278.5	.2	$11_2 - 22_2^0$
10	3418.69	29242.57	1.6	$13_2 - 28_2^0 d$	1	2510.90	39814.4	.2	$12_4 - 27_2^0$
15	3401.314	29392.00	.7	$19_2 - 87_1^0$	2	2459.80	40641.4	.3	$26_0 - 92_1^0$
4	3388.984	29498.93	1.0	$83_2^0 - 37_3$	3	2436.02	41038.1	.6	$9_3 - 18_2^0 d$
2	3365.45	29705.2	.0	$82_2^0 - 37_3$	8	2431.65	41111.9	.0	$6_4 - 29_2^0$
1	3315.32	30154.4	.3	$17_1 - 86_2^0$	4	2392.72	41780.7	— .6	$13_2 - 39_2^0$
10d	3312.27	30182.1	.0	$1_2^0 - 13_2 c$	1	2388.11	41861.3	— 2.5	$11_2 - 23_2^0$
2	3283.01	30451.1	— .7	$7_2 - 12_2^0$	5	2383.10	41949.3	.5	$12_2^0 - 15_3$
10	3246.95	30789.3	.3	$11_2 - 13_3^0$	6d	2380.98	41986.7	— .2	$9_3 - 19_2^0 d$
1	3206.85	31174.3	— .1	$13_2 - 30_2^0$	75	2354.238	42463.58	.0	$5_2 - 1_2^0$
3	3197.67	31273.6	.0	$13_2 - 31_2^0$	2	2351.90	42505.8	.5	$11_2 - 25_2^0$
1	3188.53	31353.4	1.0	$11_2 - 15_1^0$	1	2350.26	42535.4	.1	$11_2 - 26_2^0 d$
2	3175.17	31485.3	— .7	$25_4 - 90_2^0 d$	1	2343.21	42663.4	— .6	$12_4 - 31_2^0$
1	3172.02	31516.6	— 1.8	$24_3 - 89_2^0 d$	1	2295.98	43540.9	.1	$83_2^0 - 41_1$
1	3136.44	31874.1	.9	$12_4 - 19_2^0$	1	2295.57	43548.7	— .6	$13_2 - 40_2^0$
1	3130.87	31930.8	.0	$11_2 - 16_2^0$	20	2294.45	43570.0	.1	$9_3 - 20_2^0$
1	3126.90	31971.3	.4	$87_1^0 - 41_1$	2d	2285.64	43737.9	2.5	$10_1 - 23_2^0$
4	3095.46	32296.0	.1	$85_2^0 - 38_4$	1	2285.12	43747.8	.0	$82_2^0 - 41_1$
4	3080.71	32450.6	1.8	$13_2 - 32_2^0$	1	2280.77	43831.3	.6	$80_2^0 - 41_1$
1	3060.96	32660.0	.0	$84_4^0 - 38_4$	3	2280.33	43839.7	— .1	$10_2^0 - 15_3$
6	3034.73	32942.3	.2	$22_3 - 90_2^0$	15	2269.92	44040.8	.7	$11_1^0 - 16_2$
3	3022.86	33071.7	.6	$11_2 - 17_2^0$	1	2269.68	44045.4	— .1	$11_2 - 28_2^0$

TABLE II—(Continued)

Int.	$\lambda(I.A.)$	$\nu, \text{cm.}^{-1}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	Classification	Int.	$\lambda(\text{vac.})$	$\nu, \text{cm.}^{-1}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	Classification
1	2249.00	44450.4	— .5	$10_3^0 - 16_2$	15	1826.08	54762.1	— .2	$7_2 - 23_2^0$
75	2244.375	44541.98	.0	$5_2 - 2_3^0$	2	1825.59	54776.8	.2	$11_1^0 - 26_0$
20	2214.46	45143.6	.0	$4_1 - 1_2^0$	1	1806.55	55354.1	.2	$9_3 - 34_3^0$
5	2194.64	45551.3	.0	$23_3 - 93_4^0$	15	1803.95	55433.9	.1	$7_2 - 26_3^0$
1	2191.43	45618.0	— .3	$21_1 - 92_1^0$	2	1775.57	56319.9	— .1	$6_4 - 19_3^0$
3	2186.89	45712.9	— .6	$25_4 - 95_4^0$	1	1767.22	56586.1	.3	$11_2 - 39_2^0$
3	2183.31	45787.6	— .2	$12_2^0 - 17_1$	15	1759.75	56826.3	— .6	$7_3 - 15_3$
1	2178.86	45881.1	.2	$24_2 - 94_2^0$	1	1759.44	56836.3	.4	$9_3 - 35_3^0$
			— .1	$11_2 - 30_2^0$	10	1756.09	56944.7	.7	$7_2 - 28_2^0$
2	2174.24	45978.8	.3	$23_3 - 94_2^0$	12d	1741.02	57437.6	.6	$7_3^0 - 16_2$
			.9	$8_3 - 22_2^0$				— 2.4	$9_3 - 36_3^0$
8	2169.51	46078.8	.7	$11_2 - 31_3^0$	40	1740.27	57462.3	— .1	$5_2 - 3_2^0$
1	2168.08	46109.2	— .6	$23_3 - 95_4^0$	2	1739.11	57500.7	.0	$6_2^0 - 15_3$
12	2166.27	46147.8	— .0	$19_2 - 92_1^0$	75	1738.50	57520.9	1.5	$3_2 - 1_2^0$
3	2149.15	46515.3	— .9	$13_2 - 41_2^0$				— 1.2	$5_2 - 4_1^0$
1	2144.69	46612.0	.1	$22_3 - 93_4^0$	4	1736.16	57598.4	— .3	$12_2^0 - 27_1$
1d	2125.21	47039.3	.9	$22_3 - 94_2^0$	15	1727.04	57902.5	— .5	$6_4 - 20_3^0$
4d	2119.32	47170.0	.4	$22_3 - 95_4^0$	5	1724.21	57997.6	1.7	$12_2^0 - 28_2$
10	2116.34	47236.4	.0	$7_2 - 18_2^0$	8	1720.86	58110.5	— .3	$6_2^0 - 16_2$
1	2115.59	47253.1	— .2	$11_2 - 31_3^0$	8	1716.99	58241.5	— .5	$8_1^0 - 21_1$
5	2113.31	47304.1	.0	$21_1 - 94_2^0$	2	1713.68	58354.0	— .8	$11_2 - 40_2^0$
1	2112.33	47326.0	— .3	$12_4 - 33_3^0$	2	1703.98	58686.1	.1	$6_4 - 21_3^0$
1	2093.46	47752.6	.3	$18_4 - 93_4^0$	15	1692.60	59080.7	.8	$11_1^0 - 27_1$
2	2092.59	47772.4	.4	$20_5 - 95_4^0$	1	1688.02	59241.0	1.5	$9_3 - 37_3^0$
1	2089.99	47831.8	— 1.8	$19_2 - 94_2^0$	9	1681.40	59474.2	— 2.9	$11_1^0 - 28_2$
4d	2074.60	48186.6	.8	$7_2 - 19_3^0$	50	1677.90	59598.3	.5	$3_2 - 2_3^0$
1	2069.19	48312.6	1.8	$18_4 - 95_4^0$	10dd	1676.01	59665.5	.3	$8_1^0 - 24_2$
8	2058.48	48563.9	.5	$9_3 - 23_2^0$	40	1671.06	59842.3	— .3	$5_2 - 6_2^0$
10	2054.66	48654.2	— .1	$11_2 - 34_3^0$	15d	1669.82	59836.7	— .2	$10_3^0 - 28_2$
1	2037.81	49056.5	1.4	$9_3 - 24_4^0$	40	1662.72	60142.4	.0	$4_1 - 3_2^0$
2	2031.65	49205.2	.3	$9_3 - 25_2^0$	1	1658.85	60282.7	— .2	$7_2 - 33_2^0$
2	2030.44	49234.5	— .5	$9_3 - 26_3^0$	20	1654.72	60433.2	1.9	$4_1^0 - 16_2 d$
3	2029.55	49256.0	— 1.0	$10_1 - 33_2^0 d$				— 1.2	$5_2^0 - 15_3$
1	2013.69	49644.0	— .2	$12_2^0 - 23_3$	8	1653.14	60490.9	— .1	$3_2^0 - 16_2$
7	2008.63	49769.0	.2	$7_2 - 20_3^0$	20	1652.45	60516.3	— .2	$5_2 - 7_3^0$
5	2007.42	49799.0	— .8	$11_1^0 - 21_1$	60	1647.47	60699.1	.0	$2_3 - 1_2^0$
3	2006.91	49812.7	— .1	$13_2 - 42_3^0$	3	1634.68	61174.1	.6	$13_2 - 45_2^0$
3	2004.61	49868.8	.9	$9_3 - 27_2^0 d$	3	1630.30	61338.4	— 1.3	$6_2^0 - 17_1$
	$\lambda(\text{vac.})$				1	1624.63	61552.5	— .3	$7_2 - 34_3^0$
1	1981.17	50475.2	— .3	$10_3^0 - 22_3$	1	1619.64	61742.1	— .8	$9_3 - 38_2^0$
2	1970.64	50744.9	— .2	$9_3 - 28_2^0$	7	1604.62	62320.1	— 1.2	$7_3^0 - 18_4$
3	1952.16	51225.3	2.3	$11_1^0 - 24_2$	50	1599.44	62521.9	— .7	$4_1 - 6_2^0$
1	1925.43	51942.0	.5	$10_3^0 - 25_4$	3	1596.21	62648.4	1.1	$13_2 - 46_2^0$
4	1916.56	52176.8	.0	$7_2 - 22_2^0$	8	1595.73	62667.2	.0	$7_3^0 - 19_2 d$
1	1906.93	52440.3	.4	$11_2 - 37_3^0$	30	1592.93	62777.4	— .1	$2_3 - 2_3^0$
4	1905.41	52482.1	— .2	$8_1^0 - 16_2$	1	1586.36	63037.4	2.6	$7_2 - 35_2^0 e$
3	1898.30	52678.7	.2	$9_3 - 30_2^0$	5	1582.46	63192.8	.5	$10_1 - 41_2^0$
6	1894.77	52776.9	— .8	$9_3 - 31_3^0$	2	1581.76	63220.7	1.5	$8_2^0 - 26_0 d$
3	1853.46	53953.1	.2	$9_3 - 32_3^0$	3	1580.10	63287.1	1.7	$9_3 - 39_2^0$
10	1848.95	54084.8	.8	$9_3 - 33_2^0$	3b	1577.95	63373.4	— 3.2	$9_2^0 - 27_1$

TABLE II—(Continued)

Int.	$\lambda(\text{vac.})$	$\nu, \text{cm.}^{-1}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	Classification	Int.	$\lambda(\text{vac.})$	$\nu, \text{cm.}^{-1}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	Classification
1	1577.58	63388.2	.0	$6_4 - 24_2^0 d$	40	1335.08	74901.9	3.5	$3_2 - 6_2^0$
9	1575.73	63462.6	.1	$7_2^0 - 22_3$	40	1330.77	75144.5	.1	$2_3 - 5_2^0$
8	1573.12	63567.9	-.1	$6_4 - 26_3^0$	25	1326.36	75394.3	-.2	$5_2 - 12_2^0$
1	1571.36	63639.1	.2	$7_2 - 36_3^0$	2	1324.68	75490.0	.2	$1_2^0 - 16_2$
3	1570.87	63659.0	-1.2	$4_1^0 - 17_1$	4d	1323.97	75530.4	-.4	$3_2^0 - 27_1 e$
5	1569.39	63719.0	-.9	$3_2^0 - 17_1$	30	1323.22	75573.3	1.1	$3_2 - 7_2^0$
4	1565.67	63870.4	-.1	$6_2^0 - 21_1$	30	1321.04	75697.9	.0	$2_3 - 3_2^0$
5	1556.17	64260.3	-.7	$6_4 - 27_4^0$	3	1318.07	75868.5	.2	$4_1^0 - 28_2$
15	1549.85	64522.4	.1	$7_2^0 - 23_3$	2	1317.03	75928.4	.4	$3_2^0 - 28_2$
3	1547.51	64619.9	.0	$7_2^0 - 24_2$	30	1305.60	76593.2	-.1	$4_1 - 11_1^0$
			2.6	$10_2 - 42_2^0$	5	1290.07	77515.2	-.6	$7_2 - 42_2^0$
20	1540.37	64919.5	.7	$7_2^0 - 25_4$	1	1284.57	77847.1	3.5	$10_1 - 45_2^0 g$
2	1537.14	65055.9	1.5	$9_3 - 40_2^0$	30d	1280.80	78076.2	-1.9	$2_3 - 6_2^0$
15	1533.84	65195.8	-.3	$6_2^0 - 23_3$				1.7	$4_1 - 12_2^0$
12	1531.53	65294.2	.5	$6_2^0 - 24_2$	20	1277.19	78296.9	1.2	$2_3^0 - 18_4$
25	1530.49	65338.6	.2	$7_2 - 37_2^0$	7	1271.58	78642.3	.7	$2_3^0 - 19_2$
40	1527.40	65470.5	-.6	$5_2 - 8_1^0$	4	1271.12	78670.8	.3	$7_2 - 43_2^0$
12	1525.35	65558.8	.1	$6_4 - 29_2^0$	8	1270.33	78719.7	1.0	$1_2^0 - 17_1$
2	1521.59	65720.7	-.5	$3_2^0 - 19_2$	25	1269.78	78753.5	1.6	$2_3 - 7_2^0$
3	1520.41	65771.7	-.3	$11_2 - 43_2^0$	10	1258.86	79437.0	.1	$2_3^0 - 22_3$
8	1516.80	65928.2	-.6	$5_2^0 - 18_4$	2	1242.30	80495.9	-.8	$2_3 - 23_3$
7	1510.79	66190.6	-.4	$4_1^0 - 21_1$	15	1241.81	80527.6	.7	$3_2 - 8_1^0$
5	1509.45	66249.3	-1.4	$3_2^0 - 21_1$	7	1238.84	80720.7	.7	$1_2^0 - 19_2$
10	1504.48	66468.0	.4	$5_4^0 - 20_6$	2	1236.18	80894.4	1.4	$2_3^0 - 25_4$
4	1503.38	66516.8	.3	$3_2^0 - 22_3$	2	1234.53	81002.5	.7	$7_2 - 44_2^0 g$
6	1490.95	67071.4	1.4	$5_4^0 - 22_3$	9d	1230.77	81249.9	.4	$1_2^0 - 21_1$
15	1479.81	67576.3	.0	$3_2^0 - 23_3$	12	1226.75	81516.2	.9	$1_2^0 - 22_3$
10	1478.97	67614.6	.4	$4_2^0 - 24_2$	3	1209.52	82677.4	-.2	$9_3 - 45_2^0$
20	1477.75	67670.4	3.5	$3_2^0 - 24_2 d$	1	1188.35	84150.4	-1.0	$9_3 - 46_2^0 g$
3	1470.13	68021.2	.9	$9_3 - 41_2^0$	2	1180.00	84745.8	-.7	$10_1 - 80_1^0$
1	1467.78	68130.1	.3	$5_4^0 - 23_3$	8	1167.53	85650.9	-.1	$6_4 - 42_2^0$
25	1467.33	68151.0	-.1	$4_1 - 8_1^0$	8	1152.01	86804.8	.1	$6_4 - 43_2^0$
15	1459.30	68526.0	-.1	$5_4^0 - 25_4$	1	1129.16	88561.4	2.1	$3_2 - 10_2^0$
12d	1434.98	69687.4	.4	$6_4 - 34_3^0$	3	1125.16	88876.2	-.3	$7_2 - 45_2^0$
10	1405.11	71168.8	-.2	$6_4 - 35_3^0$	2	1123.99	88968.8	-.3	$3_2 - 11_1^0$
			.6	$4_1^0 - 26_0$	5	1121.90	89134.5	-1.5	$6_4 - 44_2^0$
2	1403.42	71254.5	1.2	$7_2 - 40_2^0$	1	1115.52	89644.3	.5	$9_3 - 81_2^0$
8	1393.28	71773.1	.0	$6_4 - 36_3^0$	5	1109.48	90132.3	-.6	$9_3 - 84_2^0$
25	1383.19	72296.6	.0	$4_1 - 9_0^0$	1	1106.81	90349.8	-.5	$7_2 - 46_2^0$
40	1378.96	72518.4	.2	$3_2 - 3_2^0$	8	1105.58	90450.3	.0	$3_2 - 12_2^0$
40	1377.83	72577.9	.2	$3_2 - 4_1^0$	7	1105.03	90495.3	1.3	$9_3 - 85_2^0$
10	1373.60	72801.4	.1	$2_3^0 - 15_3$	5	1090.07	91737.3	-1.7	$2_3 - 10_2^0$
20	1367.02	73151.8	1.2	$6_2^0 - 27_1$	1	1081.63	92453.0	.5	$4_1 - 16_2^0$
10	1362.19	73411.2	-.2	$2_3^0 - 16_2$	2	1068.47	93591.7	-.6	$4_1 - 17_2^0$
40	1360.46	73504.5	1.0	$5_2 - 10_2^0$	5	1068.03	93630.3	.3	$2_3 - 12_2^0$
3	1359.65	73548.3	.5	$6_2^0 - 28_2$	4	1047.19	95493.7	-.8	$5_2 - 21_2^0$
1	1359.20	73572.6	.0	$6_4 - 37_2^0$	1	1044.54	95735.9	3.5	$7_2 - 80_2^0$
20	1352.93	73913.6	.3	$5_2 - 11_1^0$	3	1043.23	95856.1	.8	$7_2 - 82_2^0$
4	1347.35	74219.7	.5	$7_2 - 41_2^0$	6	1040.96	96065.1	2.8	$7_2 - 83_2^0$
5	1336.84	74803.3	.4	$9_3 - 44_3^0$	2	1034.16	96696.9	4.0	$7_2 - 85_2^0$
20	1335.50	74878.4	-1.3	$1_2^0 - 15_3 e$	5	1029.66	97119.4	-.1	$5_2 - 22_2^0$

TABLE II—(Concluded)

Int.	$\lambda(\text{vac.})$	$\nu, \text{cm.}^{-1}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	Classification	Int.	$\lambda(\text{vac.})$	$\nu, \text{cm.}^{-1}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	Classification
3	999.26	100074	— .5	$7_3^0 - 29_3$	3	823.44	121442	3	$1_2^0 - 31_3$
8	996.94	100307	— 4	$7_3^0 - 30_2$	15	822.69	121552	1	$3_2 - 34_2^0$
10	996.51	100350	3	$5_2 - 25_2^0$	2	820.37	121843	1	$4_1 - 41_2^0$
3	996.25	100376	0	$5_2 - 26_2^0$	1	815.53	122620	4	$1_2^0 - 35_2 \text{ h}$
8	969.63	103132	— 1	$3_2^0 - 29_3$	20	812.84	123025	— 8	$3_2 - 35_2^0 \text{ g}$
1	967.99	103307	1	$4_1^0 - 30_2$	5	810.85	123327	— 3	$2_3 - 32_2^0$
8	967.43	103367	2	$3_2^0 - 30_2$	1	809.85	123480	9	$2_3 - 33_2^0$
4	964.44	103687	{	$5_2^0 - 29_3$	15	808.82	123637	0	$3_2 - 36_2^0$
				$3_2 - 13_2^0$	2	801.72	124732	1	$2_3 - 34_2^0$
1	961.88	103965	—11	$6_4 - 81_2^0 \text{ h}$	1	793.91	125959	— 2	$2_3^0 - 37_3$
2	959.26	104247	— 2	$3_2 - 15_2^0$	1	792.31	126213	0	$2_3 - 35_2^0$
10	957.36	104454	— 9	$6_4 - 84_2^0$	6	790.17	126555	— 2	$1_2 - 8_2^0$
1	956.33	104566	{	$7_3^0 - 35_2$	6	788.53	126818	{	$1_2^0 - 36_3$
				$4_1 - 28_2^0$			1	$2_3 - 36_2^0$	
				$6_4 - 85_2^0$	1	781.00	128041	1	$1_2^0 - 37_3$
2	953.95	104827	0	$3_2 - 16_2^0$	2	772.82	129396	6	$2_3^0 - 38_4$
1	943.70	105966	— 2	$3_2 - 17_2^0$	2	772.32	129480	— 3	$3_2 - 39_2^0$
1	939.94	106390	— 3	$7_3 - 86_2^0$	3	762.68	131117	— 3	$2_3 - 38_2^0$
3	935.74	106867	0	$2_3 - 13_2^0$	1	761.89	131253	1	$3_2 - 40_2^0$
4	935.10	106940	— 1	$3_2^0 - 32_2$	1	760.65	131467	— 1	$1_2^0 - 38_4 \text{ f}$
2	930.90	107423	— 3	$2_3 - 14_2^0$	3	753.79	132663	0	$2_3 - 39_2^0$
1	926.08	107982	4	$5_2 - 35_2^0$	2	745.83	134079	— 4	$2_3^0 - 40_3$
6	911.03	109766	— 1	$3_2 - 20_2^0$	5	745.06	134217	0	$3_2 - 41_2^0$
3d	904.55	110552	2	$3_2 - 21_2^0$	8	740.75	134998	— 1	$1_2 - 11_2^0$
4	903.70	110656	— 4	$6_2^0 - 37_3$	2	734.43	136160	— 1	$1_2^0 - 40_3$
6	891.47	112174	— 1	$3_2 - 22_2^0$	4	727.86	137389	2	$2_3 - 41_2^0$
2	889.82	112382	7	$5_2^0 - 36_3$	3	721.17	138664	— 5	$3_2 - 43_2^0$
2	885.86	112885	0	$5_2 - 38_2^0$	6	714.27	140003	— 3	$2_3^0 - 41_1 \text{ f}$
10	885.38	112946	— 1	$2_3 - 20_2^0$	2	710.30	140786	1	$5_2 - 81_2^0$
2	881.72	113415	0	$7_3^0 - 38_4$	6	706.13	141617	—19	$5_2 - 85_2^0 \text{ a}$
1	879.29	113728	— 2	$2_3 - 21_2^0$	5	705.00	141844	— 5	$2_3 - 38_2^0$
2	873.90	114430	3	$5_2 - 39_2^0$	2	703.85	142076	— 6	$1_2^0 - 41_2$
4	866.91	115352	{	$2_3 - 22_2^0$	3	696.96	143480	2	$4_1 - 82_1^0$
				$6_2^0 - 39_1$	1	695.93	143693	8	$4_1 - 83_2^0$
8	866.31	115432	0	$3_2 - 26_2^0$	4	693.61	144173	— 7	$2_3 - 44_2^0$
3	861.67	116054	0	$2_3^0 - 29_3$	2	660.79	151334	— 2	$5_2 - 86_2^0$
4d	859.96	116284	— 2	$2_3^0 - 30_2$	2	649.35	154000	—16	$4_1 - 86_2^0 \text{ h}$
15	855.11	116944	1	$3_2 - 28_2^0$	2	641.97	155769	— 2	$3_2 - 80_2^0$
4	846.52	118131	— 1	$1_2^0 - 29_3$	4	641.62	155856	{	$3_2 - 81_2^0$
1	844.89	118359	— 5	$1_2^0 - 30_2$					$3_2 - 82_2^0$
30	843.11	118608	{	$2_3 - 26_2^0$	3	640.76	156065	4	$3_2 - 83_2^0 \text{ h}$
				$1_2 - 4_2^0$	3	628.89	159010	—10	$2_3 - 81_2^0$
				$4_1 - 40_2^0$	2	626.93	159507	0	$2_3 - 84_2^0 \text{ h}$
4	841.21	118876	0	$3_2 - 30_2^0$	10	626.17	159700	4	$4_1 - 91_2^0$
8	839.20	119161	— 1	$5_2 - 41_2^0$	2	589.78	169555	—17	$2_3 - 86_2^0 \text{ h}$
1	838.21	119302	— 3	$2_3 - 27_2^0$	2	572.09	174798	—22	$2_3 - 88_2^0 \text{ h}$
2	837.81	119359	— 2	$2_3^0 - 31_3$	1	570.91	175159	2	$2_3 - 90_2^0 \text{ h}$
2	832.47	120124	2	$2_3 - 28_2^0$					

a Doubtful.

b Too intense for this transition.

c Wide hyperfine structure.

d Also classified in Hg II.

e Coincides with C II line.

f Forbidden by J selection rule.

g Also classified in Hg IV.

h Bloch's measurement (1).

and combining properties of the terms are consistent with the distributions in the iso-electronic spectra, chiefly Au II, Bi V, and Pb VI, and in the I and II spectra of mercury. The multiplet separation of all the identified configurations with the exception of $5d^9 6s 6p$ indicate that the coupling tends towards jj . In view of this, the nomenclature for jj coupling has been used, though its use is not to be interpreted as signifying strict jj coupling.

Mack's choice of the $J=0$ term of $5d^9 6p$, in his nomenclature 9% with the value 129080.9, has been discarded and replaced by a new one. His choice was based on the one line λ 1414.92 as the transition $5d^9 6s\ 4_1 - 5d^9 6p\ 9\%$. The excitation characteristic of this line, on the author's plates, is definitely too high to be consistent with this classification. In this analysis the line λ 1383.19 has been chosen as this transition. It is the only strong line with the proper excitation characteristic in the predicted region. This gives 130702.1 for the term value of 9% . This term value is confirmed by the presence of the lines corresponding to its combinations with the terms 10_1 and 27_1 .

The analysis is further confirmed by the hyperfine structures observed for a number of the lines in Table II. The observed structures are mainly isotopic in origin. It is to be noted that the lines which show these structures, all of which have an over-all width of approximately one frequency unit, are classified as transitions from a configuration with two $6s$ electrons to a configuration with no $6s$ electrons. This behavior is consistent with the classification since Breit's theory of isotope shifts (2) for the heavy elements predicts large structures for such transitions.

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THE PHOTODECOMPOSITION OF CHLORINE DIOXIDE IN CARBON TETRACHLORIDE SOLUTION¹

By J. W. T. SPINKS² AND H. TAUBE³

Abstract

Insolation of carbon tetrachloride solutions of chlorine dioxide initiates a thermal decomposition, the magnitude of which may exceed that for the photo-reaction with low light intensity. This thermal decomposition is inhibited by keeping the solutions at 3° C. or by adding water.

In contradiction to the findings of other investigators, it is found that chlorine and oxygen are not the only products of photodecomposition. As products of the photodecomposition of chlorine dioxide at the wave-lengths 3650 and 4360 Å, the oxides Cl_2O , Cl_2O_6 , and Cl_2O_7 as well as chlorine and oxygen appear. The quantum efficiency at λ 3650 Å is 2, and at 4360 Å, 1.

In the unsensitized decomposition, concentration effects are observed which are greatly decreased when the solutions are stirred.

In the bromine sensitized decomposition with 5460 Å, there is less chlorine monoxide but relatively as much Cl_2O_6 and Cl_2O_7 formed as in the unsensitized reaction.

In the sensitized decomposition the quantum yield is independent of the concentration of chlorine dioxide, but depends on the light intensity. The observed quantum yield for the sensitized reaction is 0.2 to 0.3.

Mechanisms for the photo-reactions have been proposed.

Introduction

Gaseous chlorine dioxide decomposes at a measurable rate above 30° C., but at temperatures of from 50° to 60° C., the decomposition proceeds explosively; Cl_2O_6 is an intermediate product in the thermal decomposition (26). Luther and Hoffmann (15, 16) have made a study of the thermal decomposition of chlorine dioxide in carbon tetrachloride solution. Pure chlorine dioxide solutions were found to be stable in the dark; previous insolation or the addition of chlorine monoxide initiates a slow thermal decomposition.

In the visible region of the spectrum, chlorine dioxide shows band absorption that begins at 5225 Å and continues to 2000 Å (8, p. 709; 28). At 3750 Å the lines become diffuse; this indicates predissociation. The bands may be extrapolated to a convergence limit at 2560 Å, corresponding to a dissociation of the chlorine dioxide to $\text{ClO} + \text{O}(^1\text{D})$. The energy required for the dissociation



corresponds to a wave-length 4360 Å. It is of course possible that predissociation takes place up to 4360 Å even though diffuse bands are not observed.

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On insolation of gaseous chlorine dioxide, Booth and Bowen (3) obtained a brown liquid which was later identified as Cl_2O_6 (2). Finkelnburg and Schumacher (8, p. 709) investigated the reaction, using λ 4360 and 3130 Å.

Spinks and Porter (27, p. 269) found the photodecomposition with dry gases to be complicated. A chain mechanism was indicated since the quantum yield was found to be about 12. By using moist gases, results were reproducible, since active groups, presumed to be ClO_3 , ClO , and Cl_2O_3 , were then removed by the water. With moist gases and wave-lengths 4360 and 3650 Å, quantum yields of 3.1 and 3.7, respectively, are obtained. For the bromine sensitized reaction, with moist gases and λ 5460 Å, the quantum yield was found to be equal to the yield when 3650 Å was used.

In carbon tetrachloride solutions, using blue and violet light, Bowen (4) found $\gamma = 1$, but the light measurements were not very accurate. A slight thermal reaction was reported. Nagai and Goodeve (17), using λ 4100 to 4200 Å, obtained a quantum yield of 2. They observed a rapid thermal reaction and made their calculations on the assumption that the thermal and photo-reactions proceed independently. In contrast to the reaction in the gas, it was claimed that no Cl_2O_6 is formed. Bowen (5) and Bowen and Chung (6) repeated the study with carbon tetrachloride and water solutions, and used light of wave-length varying from 3000 to 4360 Å. In carbon tetrachloride, the quantum yield was found to be equal to 2 up to 4200 Å; at 4360 Å it was found to be 1; for water solutions it increased from 0.2 at a wave-length of 4360 Å to 1 for λ 3000 Å.

Since the line 5460 Å does not possess sufficient energy to cause the dissociation



it was hoped that by studying the bromine sensitized decomposition, using this wave-length, further significant information about the photodecomposition of chlorine dioxide might be obtained. Since our experiments differed in important respects from published work on the subject of the photodecomposition of chlorine dioxide, the original study was extended to include the unsensitized decomposition with wave-lengths 4360 and 3650 Å.

The work reported here embraces a study of the thermal decomposition, an investigation of the reaction products of the photodecomposition, measurement of the quantum yield, and a study of the influence of light intensity and of concentration of the reactants on the rate of decomposition.

Experimental

Preparation of Materials

Carbon Tetrachloride. U.S.P. carbon tetrachloride was filtered, shaken with concentrated sulphuric acid, washed with alkali, and dried with calcium chloride. Chlorine dioxide was passed in and the solution exposed to light from a 100 watt bulb for a period of about four days, more chlorine dioxide being passed in as it was decomposed. The chlorine and chlorine dioxide were then washed out with concentrated alkali and the carbon tetrachloride

was dried over phosphorus pentoxide. After drying for some time, it was distilled in an all-glass apparatus from phosphorus pentoxide, the end fractions being discarded.

Untreated U.S.P. carbon tetrachloride, as well as Mallinckrodt's c.p. carbon tetrachloride showed anomalous effects. In runs with such carbon tetrachloride, thermal decomposition at 3°C ., large change in total halogen (calculated as described below) and large decrease in light absorption were noticed. All batches of carbon tetrachloride subjected to a rigorous treatment with chlorine dioxide gave comparable results.

Bromine. In the earlier experiments, a c.p. grade of bromine was used. For the later work, this grade of bromine was treated by distilling from potassium bromide and potassium bromate and from phosphorus pentoxide. No difference in the results obtained by using either grade of bromine could be observed.

Chlorine Dioxide. This gas was prepared by the method of Bray (7). Potassium chlorate (3 gm.) and crystalline oxalic acid (12 gm.) were ground in a mortar, and 1.5 cc. of water was added. The mixture was then heated at a temperature of 55° to 65°C . The gas evolved was bubbled through saturated sodium bicarbonate, pre-dried with sulphuric acid, then passed over phosphorus pentoxide into dry, purified carbon tetrachloride. In all cases the chlorine dioxide contained about 2 mole per cent of chlorine. The solutions were prepared just before use and were kept, carefully shielded from light, at 0°C .

Apparatus

The light source was a constant pressure, quartz mercury lamp, consuming 1.8 amp. at 220 volts. For some experiments a vacuum quartz mercury lamp consuming 2.5 amp. was used. The light from the latter is very intense but flickers excessively. The light filters employed were: for 5460 \AA , a combination of Corning Nonex, heat resisting yellow, 2.8 mm. thick, and a Corning Didymium glass 4.97 mm. thick; for 3650 \AA , a Corning red purple ultra filter, 3.9 mm. thick; for 4360 \AA a cobalt glass and 2 cm. of a solution of 40 gm. of sodium nitrite in 100 cc. of water.

For the experiments on quantum yields, where accurate light measurements are necessary, the optical arrangement shown in Fig. 1 was used. The arrangement of lenses and apertures was such that a fairly homogeneous beam, slightly convergent, with a cross section at the face of the thermopile of 1.5 cm. in diameter, was obtained. The light measuring instrument was a Moll surface thermopile (receiving cone stepped down, active surface 2 cm. in diameter) connected in series with a sensitive galvanometer.

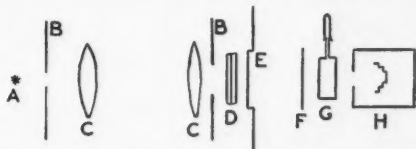


FIG. 1. A, mercury lamp; B, apertures; C, lenses; D, filters; E, bath; F, shutter; G, cell; H, thermopile.

Deflections were read by means of an optical lever, radius 1.2 m. The thermopile was calibrated against two Bureau of Standards carbon filament lamps. One millimetre of deflection corresponds to 1.14×10^{-5} watts falling on the face of the thermopile. The calibration and optical systems were checked by measuring the quantum yield of the uranyl oxalate decomposition with λ 3650 Å, the value for this reaction being accurately known (28). The results obtained are described under the heading "Measurement of the Quantum Yield."

For the other experiments, in order that there would be a measurable decomposition in a short time, a more intense beam was used. This was obtained by condensing the light from the lamp, without a diaphragm, by means of a 500 cc. Pyrex flask, filled with water and at a distance of 2 cm. from the lamp, and a lens at a distance of 1 or 2 cm. from the flask.

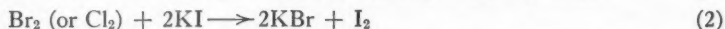
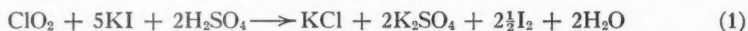
The reaction cell employed was of Suprax glass, 2 cm. in thickness and 5 cm. in diameter, fitted with a ground glass cap, and over this a tube and stopper to exclude water. The volume of the cell was about 29.5 cc. The bulbs used to determine the initial concentration and the thermal change were blown from soft glass, and were also fitted with ground glass caps. The joints were sparingly lubricated with a brominated grease. Experiments showed that there was no loss of oxidizing material over a 24-hr. period.

For the low temperature work, the solutions were exposed to the light in a small insulated bath fitted with two glass windows. Ice was kept on the surface of the water and the cell was thus maintained at a temperature of about 3° C.

Procedure and Method of Analysis

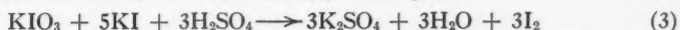
The chlorine dioxide solution, prepared as described above, was dispensed from the containing vessel into the cells by means of dry compressed air. In the early runs, when the conditions under which the thermal change took place were being studied, three portions were used: one to obtain the initial concentration, one to measure the thermal change, and one to measure the change on insolation. The amounts of solution used were obtained by weighing.

To analyze the solutions, the liquid was forced into potassium iodide solution by means of a siphon. All oxidizing material was removed by blowing with dry compressed air. To the resulting solution was added standard acid in excess of that required in Reaction (1).



The iodine liberated in these reactions is determined by titration with 0.1 *N* sodium thiosulphate. Reaction (1) uses up acid quantitatively; thus the chlorine dioxide can be obtained from the amount of acid which disappeared. If this result is compared with the total iodine liberated, the amount of chlorine

plus bromine may be obtained. The excess acid was determined by adding excess potassium iodate, and Reaction (3) takes place.



The liberated iodine was again titrated with 0.1 *N* sodium thiosulphate and gave a measure of the excess acid which had been added. Thus the amount of acid used in Reaction (1) could be calculated.

Throughout this report, the chlorine dioxide used in a run, the amount left after decomposition, and the amount decomposed is expressed in terms of the corresponding titre for 0.1 *N* sodium thiosulphate divided by 5. Multiplying by 10^{-4} gives the actual number of moles of chlorine dioxide involved. The chlorine and bromine are expressed in terms of the 0.1 *N* sodium thiosulphate titre. These units are adopted since equal titres then represent equal amounts of halogen.

The following was used as a check on the analysis. For the same weight of solution in each of the cells,

$$\frac{\text{ClO}_2 \text{ titre}}{5} + (\text{Cl}_2 + \text{Br}_2) \text{ titre,}$$

(both in cubic centimetres of 0.1 *N* sodium thiosulphate) should be a constant, since this represents the total halogen present, none of which is lost.

To check the method of handling the solutions, bulbs were filled consecutively and analyzed. An example of the type of results obtained is given in Table I. From this and similar experiments it was concluded that the method of handling the solutions was satisfactory.

TABLE I

Cell	ClO_2 titre	Cl_2	Total halogen
1	22.60	0.32	4.84
2	22.65	0.37	4.92

Experiments done during the latter part of this work indicated that Cl_2O , Cl_2O_6 , and Cl_2O_7 are present in the decomposition mixture. Chlorine monoxide reacts with potassium iodide, Cl_2O_7 gives perchloric acid in water, and Cl_2O_6 may give chloric acid and perchloric acid. Thus the change in titre obtained by the potassium iodide-potassium iodate method outlined above does not represent the change in chlorine dioxide. A method was therefore devised whereby the chlorine and chlorine dioxide can be estimated apart from Cl_2O , Cl_2O_6 , and Cl_2O_7 . The method included the determination of these oxides from the products of their reaction with water.

The procedure adopted for complete analysis is as follows. By means of a siphon, the decomposition mixture is transferred quantitatively to a bottle containing 10 cc. of 0.1 *N* hydrochloric acid in 50 cc. of water. The stop-cocks on the bottle are closed and the mixture is shaken vigorously, then kept in the dark until the mist has settled. Air is drawn through the bottle and through a series of three tubes containing a solution of potassium iodide.

The chlorine dioxide and chlorine carried off by the air are absorbed by the potassium iodide solution. Aspirating for one to one and one-half hours is sufficient to remove chlorine dioxide and chlorine. The amounts of chlorine dioxide and chlorine are determined by the usual titration of the potassium iodide solutions obtained.

The solution in the bottle now contains hydrochloric acid, chloric acid, and perchloric acid. The last two are formed in the reaction of Cl_2O_6 and Cl_2O_7 with water. The hypochlorous acid formed in the reaction of chlorine monoxide with water is removed by the foregoing treatment according to the reaction



The amount of hydrochloric acid lost from the solution gives a measure of the hypochlorous acid that was present.

The carbon tetrachloride is separated from the water layer in a separatory funnel, and the water solution is neutralized with standard base, phenolphthalein being used as an indicator. The end point is quite stable in chloric acid and perchloric acid of the concentrations obtained here. The amount of base required gives the amount of $\text{HCl} + \text{HClO}_3 + \text{HClO}_4$ that was present. The neutralized solution is slightly acidified with sulphuric acid and the Cl^- precipitated with a solution of silver sulphate. The silver chloride is collected and weighed; the amount gives a measure of the hydrochloric acid that was left after the aspiratory process. Since the amount of hydrochloric acid added is known, the amount lost and thus the hypochlorous acid that was present can be calculated. Subtraction of the acid equivalent of the silver chloride from the acidity determined in the base titration gives the $\text{HClO}_3 + \text{HClO}_4$ that was present.

The excess Ag^+ in the filtrate from the chloride determination is precipitated with sodium chloride and the silver chloride filtered off. The solution is neutralized and evaporated to about 75 cc. The ClO_3^- is determined by the ferrous sulphate method, using 0.1 *N* potassium permanganate to determine the excess Fe^{++} used. The perchloric acid can now be calculated by difference.

If the solution analyzed contains bromine, it is sometimes necessary to extract the water layer obtained from the carbon tetrachloride separation with a small amount of carbon tetrachloride. The bromine does not come over completely even after aspirating for one and one-half hours.

The following checks on this procedure have been applied.

Two samples of a solution of chlorine dioxide in carbon tetrachloride were weighed. One sample was analyzed directly by the potassium iodide-potassium iodate method. The following amounts of chlorine dioxide and chlorine were found: ClO_2 , 2.67; Cl_2 , 0.27. The other sample was treated exactly as outlined in the procedure for complete analysis. For the same weight of solution as above: ClO_2 , 2.67; Cl_2 , 0.16. Amount of hydrochloric acid added, 10.02 cc.; amount of hydrochloric acid found, 10.00 cc. No hypochlorous

acid, chloric acid, or perchloric acid was found. A second experiment gave for direct titration: ClO_2 , 8.10; Cl_2 , 0.32. For complete analysis: ClO_2 , 8.08; Cl_2 , 0.20. Added 9.80 cc. HCl ; found 9.79 cc. HCl .

These experiments show:

- (1) That the method is quantitative for chlorine dioxide; none of the chlorine dioxide remains as oxyhalogen acids,
- (2) That there is no appreciable loss of hydrochloric acid by entrainment or evaporation.

Experiments with chlorine monoxide in water showed that the removal of hypochlorous acid is complete if excess hydrochloric acid is present. No oxidizing material remains after aspirating for one and one-half hours. Mr. R. Ralston has shown by test runs in this laboratory, using chlorine monoxide many times (about ten) more concentrated, that only about 1% of chlorine monoxide comes over as the oxide, the rest reacting with water to give hypochlorous acid, which then reacts with hydrochloric acid according to Reaction (4).

Experiments with chloric acid (prepared from barium chlorate and sulphuric acid) and hydrochloric acid mixtures showed that at the concentrations obtained in our runs no oxidizing material is carried over in the aspiratory process. A mixture subjected to the procedure outlined above gave an analysis for chloric acid agreeing to within 3% of what was added.

Finally, the ClO_4^- was determined by the titanous sulphate method (23) and good agreement with the value calculated by difference was obtained. For example, in one experiment: $\text{ClO}_4^- = 1.52 \times 10^{-4}$ moles, by titanous sulphate method; by difference, $\text{ClO}_4^- = 1.44 \times 10^{-4}$ moles. In another experiment, $\text{ClO}_4^- = 2.96 \times 10^{-4}$, by reduction; by difference = 2.99×10^{-4} moles. It was found necessary to boil for two and one-half to three hours to effect complete reduction of the ClO_4^- by Ti^{+++} .

As the amounts dealt with in the water extract are small, the percentage error in the determinations is quite high, usually about 5%.

In spite of the formation of considerable amounts of Cl_2O_6 and Cl_2O_7 , the direct titration of the decomposition mixture during the early work did not show any significant discrepancies in the total halogen balance. While this is at first surprising, consideration of a hypothetical case shows that the formation of relatively large amounts of Cl_2O_6 or Cl_2O_7 produces only small discrepancies in the halogen balance.

Experimental Results

Preliminary Experiments: Experiments on Thermal Decomposition

All results, except where otherwise stated, were obtained with carbon tetrachloride purified by the method described.

At 20° C. the thermal decomposition was particularly troublesome. Experiments soon showed that if the solutions prepared were kept carefully shielded from light they would decompose only very slowly, in agreement with observations of Luther and Hoffmann (15).

In the first experiments the light was measured with the thermopile behind the cell and the incident intensity obtained by substituting a similar cell filled with carbon tetrachloride. The estimation of chlorine dioxide and chlorine was made by means of the direct potassium iodide-potassium iodate method.

It was found that solutions of chlorine dioxide in carefully purified carbon tetrachloride which have not been exposed to light are thermally stable, *e.g.*, no measurable decomposition takes place in six hours at 20° C. At the concentrations used, λ 5460 Å does not bring about any decomposition of chlorine dioxide (the absorption of this wave-length at the concentrations used is less than 0.5%), but on the addition of bromine, λ 5460 Å is absorbed and a sensitized reaction takes place. When the solution was insolated for 10 min. and then kept in the dark for three hours at 20° C., a large thermal reaction was initiated. In another experiment water was added to the solution in the cell. The mixture was insolated for 10 min. and then left in the dark for three hours at 20° C. No thermal change took place. In a further experiment, the solution was insolated for 10 min. and then kept for three hours at 3° C. Again there was no appreciable thermal decomposition. These experiments demonstrated that light initiates a thermal decomposition at 20° C. which does not, however, take place in wet carbon tetrachloride or at 3° C. With wet carbon tetrachloride, the solutions become cloudy on insolation; this makes accurate light measurements impossible.

The unsensitized reaction at 3650 Å shows the same effect, *i.e.*, a thermal reaction is initiated by 10 min. insolation at 20° C. but not at 3° C. The remainder of the work was therefore carried out at 3° C. where thermal decomposition is negligible.

Products of the Photodecomposition

Previous workers on the photodecomposition of chlorine dioxide in carbon tetrachloride solution have stated that chlorine and oxygen are the only products of the reaction. Bowen (5) examined insolated chlorine dioxide solutions analytically to determine whether Cl_2O_6 was formed, and he reported negative results.

Since Cl_2O_6 is formed in the gaseous photodecomposition of chlorine dioxide (2, 27, p. 269), it was thought worthwhile to look for evidence of it in the photo-reaction in solution. Accordingly, a solution of chlorine dioxide at 3° C. was strongly insolated with light of wave-length 3650 Å. The reaction mixture was forced into water and shaken up. A heavy mist was observed, identical in appearance with that which forms when Cl_2O_6 reacts with water. The chlorine dioxide and chlorine were removed from the water extract by aspirating air through for a period of three hours. The resulting solution had the odor of chlorine water but gave no precipitate with silver nitrate. It oxidized potassium iodide but did not reduce potassium permanganate. Thus ClO^- was indicated, and ClO_2^- and Cl^- were concluded to be absent. ClO^- was further confirmed since a small amount of solution decolorized indigo dissolved in concentrated sulphuric acid.

To test for ClO_3^- and ClO_4^- , a known amount of hydrochloric acid was added to the remainder of the water extract and the solution aspirated until no more oxidizing material passed over. This oxidizing substance was absorbed in potassium iodide and the amount determined. Thus, it was possible to calculate the hydrochloric acid which had reacted with the hypochlorous acid and came over as chlorine. The solution was now neutralized with standard potassium hydroxide. Acid in excess of the hydrochloric acid was observed to be present. This solution was evaporated to a small volume. Microscopic examination of the crystals obtained showed potassium chlorate and perchlorate. The presence of ClO_4^- was also demonstrated by the characteristic crystals obtained when a drop of 2% brucine solution was added to a drop of the test solution on a microscope slide. The outer part of the drop formed a brown ring, which is also characteristic of ClO_3^- . The tests were compared with similar tests on pure substances.

These qualitative tests showed that chloric acid, perchloric acid and hypochlorous acid were present in the water extract of the reaction mixture. By application of the method for complete analysis, quantitative estimation of the amounts was possible.

Table II shows the type of results obtained on carrying out the complete analysis.

Throughout this report the amounts of these acids found will be given in terms of the amount of 0.1 *N* acid they represent. This converts them to the same basis, as regards halogen, as the figures for chlorine dioxide.

TABLE II
COMPLETE ANALYSIS, HIGH LIGHT INTENSITY

Run No.	Amount ClO_2	Temp., °C.	Time, min.	ΔClO_2	HClO	HClO_3	HClO_4
1	18.54	3	240	13.82	1.64	0.66	2.34
2	8.14	3	60	3.74	0.75	0.41	0.55
3	14.51	3	60	4.00	1.02	0.55	0.54
4	17.43	20	60	4.33	0.89	0.20	0.60
5	21.18	3	240	6.14	1.48	0.71	1.48
6	10.66	3	25	6.08	1.29	0.52	1.16

In the experiments listed in Table II the $\text{HClO}_3 + \text{HClO}_4$ found represents about one-quarter of the total halogen of the chlorine dioxide which decomposed, while the hypochlorous acid represents about one-fifth. The table illustrates clearly the importance of using the complete analysis.

As possibilities to account for these acids in the water extract there are the oxides Cl_2O , Cl_2O_3 , Cl_2O_6 , and Cl_2O_7 .

Cl_2O_3 (27, p. 269) is assumed to react with water to give two moles of chlorous acid which interact to give equal amounts of hypochlorous acid and

chloric acid. Since the presence of these acids is observed, it might be supposed that Cl_2O_3 was present. This oxide, however, requires equal amounts of hypochlorous acid and chloric acid; *i.e.*, chloric acid in excess of hypochlorous, if Cl_2O_6 is present. In all our experiments the chloric acid is less than the hypochlorous acid. Hence, it is concluded that the formation of the oxyhalogen acids found is better explained by the presence of other oxides.

The hypochlorous acid can readily be explained by the presence in the decomposition mixture of chlorine monoxide which reacts with water to give this acid.

The $\text{HClO}_3 + \text{HClO}_4$ can be explained by the reaction of Cl_2O_6 with water. Experiments have shown that when Cl_2O_6 reacts with water, chloric acid and perchloric acid are formed; perchloric acid always being in excess of the chloric acid. This relation was accounted for by the decomposition in the reaction zone of chloric acid to perchloric acid and ClO_2 , by means of the strongly dehydrating Cl_2O_6 . However, when, as in our experiments on the decomposition of chlorine dioxide, there is a dilute solution of Cl_2O_6 in carbon tetrachloride, this mode of action would not apply, and the Cl_2O_6 would be expected to yield equal quantities of chloric acid and perchloric acid. This possibility was tested by preparing a dilute solution of Cl_2O_6 in carbon tetrachloride by bubbling ozone through a cold solution of chlorine dioxide in carbon tetrachloride. The resulting solution was treated as in the procedure for complete analysis. Found: HClO_3 , 0.22; HClO_4 , 0.24. This experiment demonstrated that Cl_2O_6 acts under our conditions as the mixed anhydride of chloric acid and perchloric acid. Additional support is lent to this by the fact that in some experiments (Table II, Experiments 2 and 3) using high concentrations of chlorine dioxide and small fractional decomposition, the ClO_3^- is very nearly equal to the ClO_4^- . This is what would be expected if Cl_2O_6 were formed and if none of it were decomposed to Cl_2O_7 .

Thus, it can reasonably be assumed that the chloric acid represents the Cl_2O_6 present. The perchloric acid in excess of chloric acid can be assumed to be formed from Cl_2O_7 . This oxide is formed on continued insolation of gaseous chlorine dioxide (3). It would be expected that the solution in carbon tetrachloride would show similar behavior.

Of these oxides, Cl_2O and Cl_2O_6 undergo further decomposition. Experiments 1, 2, and 3 in Table IX indicate that the amount of ClO_3^- increases from zero, at the beginning, to a maximum. An experiment was performed in which a solution of chlorine dioxide was insolated with 3650 Å. The absorption of green light by this solution was determined at intervals during the decomposition.

Experiment 1 N (*N* will be used to characterize all experiments not tabulated.)

ClO ₂ initial, 14.60			ClO ₂ final, 0.31				ΔClO ₂ , 14.29			
Time, min.	0	30	45	60	75	90	120	180	255	315
Per cent absorption for 5460 Å	0.2	3.0	3.5	3.7	3.4	4.4	2.1	2.2	1.4	0.3

The absorption rises to a maximum, then falls off. The amount of ClO_3^- formed during a decomposition shows the same behavior. Cl_2O_6 would be expected to absorb 5460 Å strongly (11), and it may reasonably be assumed that the change in absorption is due to this oxide. The absorption coefficient of gaseous chlorine monoxide for 5460 Å is about 0.00003 (9) in terms of millimetres of pressure and centimetres of absorbing path. Chlorine monoxide equivalent to 2 cc. of 0.1 *N* hypochlorous acid per cell would give an absorption of only 0.5%. This is about the maximum amount of chlorine monoxide ever obtained, which cannot therefore explain the above absorption.

The value of the extinction coefficient of Cl_2O_6 in carbon tetrachloride solution for λ 5460 Å is not known. Goodeve and Richardson give values for the extinction coefficient of liquid Cl_2O_6 up to the wave-length 5700 Å. The coefficient increases rapidly up to this point, where a value of 63 (moles per litre, centimetres of absorbing path) is reached. If a value of 100 for the extinction coefficient at 5460 Å is assumed, calculation shows that Cl_2O_6 equivalent to 0.5 cc. of chloric acid in the cell would show an absorption of 50% for green light. The maximum absorption observed is about 4%. On the assumption of an absorption coefficient of 10 for Cl_2O_6 , the absorption would be about 6% for the amount represented by 0.5 cc. of chloric acid. Since the extinction coefficient may increase or decrease with decreasing wave-length, the above evidence is inconclusive, but is quite compatible with the presence of Cl_2O_6 . The facts that Cl_2O_6 is formed in the gaseous decomposition and that in the experiments with low percentage decomposition HClO_3 and HClO_4 are formed in equal amount still incline the authors to the conclusion that Cl_2O_6 is present.

Experiment 1 *N*, which was carried out to complete decomposition, yielded at the end of the run no chloric acid and no hypochlorous acid, but 2.99 cc. of 0.1 *N* perchloric acid. This value was checked by means of the titanous sulphate reduction. Thus it appears that the Cl_2O and Cl_2O_6 are themselves decomposed and only Cl_2 , O_2 , and Cl_2O_7 are obtained as end products. Cl_2O_7 does not absorb 3650 Å (12) and appears to be quite stable. About one-fifth of the chlorine dioxide decomposed went to form this oxide.

Experiments conducted at 20° and 30° C. give analyses similar to the above, except that the chloric acid is much less, or even absent. This behavior would be expected of Cl_2O_6 ; it might equally well apply to Cl_2O_3 .

Experiment 2N: 30° C., intense beam, complete analysis. ClO_2 initial, 12.61; ΔClO_2 , 10.79; HClO , 0.77; HClO_4 , 2.27; HClO_3 , 0.00.

Experiment 3N: 20° C., intense beam, complete analysis. ClO_2 initial, 19.87; ΔClO_2 , 10.89; time, 1.5 hr. HClO , 1.91; HClO_3 , 0.20; HClO_4 , 2.15.

Experiment 4N: 3° C. This is added for comparison with 3*N*. It was done with the same light beam. ClO_2 initial, 27.36; ΔClO_2 , 11.45; HClO , 2.25; HClO_3 , 1.14; HClO_4 , 1.87.

Comparison of Experiments 3*N* and 4*N* shows that whereas the amount of chloric acid is much less at 20° C. than at 3° C., that of hypochlorous acid

shows little difference at the two temperatures. It appears that at 30° C. the Cl_2O_6 is decomposed as rapidly as it is formed; at 20 °C. it is also decomposed rapidly.

Decomposition with the wave-length 4360 Å yields reaction products of the same kind in about the same relative amounts as are obtained with 3650 Å. (See Experiment 8N.)

The results of complete analyses on decomposition mixtures from the bromine sensitized reaction with wave-length 5460 Å are given in Table III.

TABLE III
BROMINE SENSITIZED DECOMPOSITION OF CHLORINE DIOXIDE SOLUTIONS (λ 5460 Å),
COMPLETE ANALYSIS

Run No.	Amount ClO_2	Temp., °C.	Time, min.	Decomp. ClO_2	ClO^-	ClO_2^-	ClO_4^-
1	20.50	3	180	3.74	0.34	0.30	0.64
2	10.00	3	180	2.91	.20	.35	.67
3	10.16	3	180	1.63	.30	.23	.37
4	9.32	3	250	3.92	.03	.11	.68

In the bromine sensitized decomposition, the chloric acid and perchloric acid represent about one-fifth of the total halogen of the chlorine dioxide decomposed. The amounts of hypochlorous acid found, though small, appear to be definite. In Experiment 4 the bromine content was very high (85% abs.). The results show that the amount of Cl_2O_6 is less in this experiment than in the others and may mean that Cl_2O_6 undergoes a bromine sensitized decomposition. Experiments by Mr. Ralston in this laboratory have shown that chlorine monoxide undergoes a bromine sensitized decomposition, and consequently only small amounts of this oxide would be able to accumulate.

Measurement of the Quantum Yield

The experiments on the thermal decomposition showed that it would be necessary to conduct the work at about 3° C. For the measurements in Table IV a small bath, well insulated and of sufficient size to accommodate the thermopile and cell, was constructed. The ice was contained in cans; this kept the water optically clear. The thermopile was placed as close to the cell as possible. A light beam, the same as that used in the early quantum yield experiments, but of greater cross section, was used.

TABLE IV
COMPLETE ANALYSIS, 3° C.

Exp. No.	Amount ClO_2	ΔClO_2	Time, min.	Amount light absorbed, mm.	γ
1	6.57	2.88	480	140	2.04
2	11.87	2.81	420	143	2.23

Scattered light was estimated by settings of the thermopile. The amount was about 10% of the total.

To check these values, a measurement of the quantum yield of the uranyl oxalate decomposition was made. The value for this reaction is accurately known and the procedure has been described in detail (28). No departure was made from the procedure outlined there. The oxalic acid concentration used was about 0.1 *M*. The solutions were stirred continuously. Using the same beam and applying the correction for scattering, we obtained a value of 0.55 for γ . The accepted value is 0.492. Correcting our values for γ_{3650} by multiplying by the ratio $\frac{0.492}{0.55}$, values of 1.83 and 1.99 for Experiments 1 and 2 respectively are obtained. Better agreement in the values need not be expected. The values obtained agree with those of Nagai and Goodeve ($\gamma = 1.98$) and Bowen and Cheung ($\gamma = 2.00$).

To determine whether there is a large difference in the decomposition for the same amount of light absorbed at 3° and at 20° C., the experiments listed in Table V were performed.

TABLE V
HIGH INTENSITY, DIRECT ANALYSIS

Series	Run No.	Amount ClO_2	Temp., °C.	Time, min.	ΔClO_2	Ratio
1	1	2.09	19.5	45	0.788	1.263
	2	1.92	3.5	45	0.624	
2	1	3.78	19.5	45	2.904	1.172
	2	3.63	3.5	45	2.482	

Series 2 was done with a light intensity about four times as great as that in Series 1. These experiments show that probably the only difference in the reaction at the two temperatures is that at 20° C. the photodecomposition is accompanied by a thermal reaction. At the light intensity used, this is slow compared to the light reaction.

An experiment was performed in which the set-up for the intense beam was used. The decomposition of a chlorine dioxide solution exposed for a definite time was determined by the method for complete analysis. Then a solution of uranyl oxalate was exposed for a certain length of time with the same optical set-up. The absorption of the solution was measured, and assuming the same quantum yield for the uranyl oxalate decomposition at the high intensity as at the low, we could calculate the quantum yield of the reaction with λ 3650 Å. An experiment on the bromine sensitized decomposition was done at the same time to compare γ_{3650} with γ_{5460} . The experiments and results are reported below.

Experiment 5N. Decomposition of chlorine dioxide with λ 3650 Å; complete analysis; 3° C.; high intensity beam; time, 64 min. ClO_2 initial, 13.40; ΔClO_2 , 12.53; % abs. = 96 (for comparison with uranyl oxalate experiment). Rel. $I_{\text{abs.}}$ = 212 (for comparison with bromine sensitized decomposition).

Experiment 6N. Decomposition of uranyl oxalate with λ 3650 Å; beam as above; 22° C.; time, 64 min.; change in oxalic acid is equivalent to 13.13 cc. 0.04896 *N* potassium permanganate. % abs. of solution, 44.4; γ_{3650} calculated from this data = 2.15. The agreement with the results obtained with the small beam is fairly good.

Experiment 7N. Bromine sensitized decomposition of chlorine dioxide by λ 5460 Å: 3° C.; beam as above; time, 64 min. ClO_2 initial, 12.42; ΔClO_2 , 1.77; Rel. $I_{\text{abs.}}$, 185; % abs., 80; $\frac{\gamma_{3650}}{\gamma_{5460}} = 9.23$.

This experiment places the quantum yield for the bromine sensitized reaction with high bromine concentration at $\frac{2.15}{9.23} = 0.233$.

Another experiment was performed in which the quantum yields at 3650 Å and at 5460 Å were compared (Table VI).

TABLE VI
DIRECT ANALYSIS, HIGH INTENSITY

Exp. No.	Amount ClO_2	Temp., °C.	λ , Å	Rel. no. quanta abs.	Decomposition	Relative γ
1	13.20	3	3650	4.149	7.94	7.50
2	13.20	3	5460	3.684	0.94	1.00

The absorption of the bromine sensitized solution was about 45%. This experiment places γ for a solution with a moderate concentration of bromine at $\frac{2.00}{7.50} = 0.27$.

Further values of γ for the sensitized decomposition of chlorine dioxide solutions, using λ 5460 Å, are given in Table VII. Experiments reported later will show that there is a real variation in the values of γ for the bromine sensitized decomposition.

A comparison of γ_{3650} with γ_{4360} was also made.

TABLE VII
DIRECT ANALYSIS. QUANTUM YIELDS
FOR THE BROMINE SENSITIZED REACTION
(λ 5460 Å)

Initial ClO_2	Per cent light absorbed (by Br_2)	γ
1.934	48.7	.22
6.104	47.0	.28
6.008	48.0	.32
1.732	14.6	.28
1.560	72.0	.19
6.788	77.3	.22

Experiment 8N: Temp., 3° C., high light intensity, complete analysis.

$\frac{I_{\text{abs. 3650}}}{I_{\text{abs. 4360}}} = 1.31$. With 3650 Å: ClO_2 initial, 9.63; ΔClO_2 , 4.30; time, 40 min. ClO^- , 0.89; ClO_3^- , 0.25; ClO_4^- , 0.75.

With 4360 Å: ClO_2 initial, 9.61; ΔClO_2 , 3.19; time, 60 min. ClO^- , 0.66; ClO_3^- , 0.33; ClO_4^- , 0.49. $\frac{\gamma_{3650}}{\gamma_{4360}} = 1.86$.

This experiment places the quantum yield of the decomposition with λ 4360 Å at about 1. This value is in agreement with the published value (6).

To sum up, on the basis of this work the quantum yield of the unsensitized decomposition with 3650 Å is 2.0; with 4360 Å, 1.0; and that of the bromine sensitized decomposition with 5460 Å is 0.2 to 0.3.

EXPERIMENTS ON THE KINETICS OF THE UNSENSITIZED DECOMPOSITION WITH $\lambda = 3650$ Å

Effect of Concentration of Chlorine Dioxide

These experiments show that increasing the concentration increases the amount of decomposition per unit of light absorbed (compare Table XII).

TABLE VIII
HIGH INTENSITY, I_{abs} , SAME IN EACH CASE, COMPLETE ANALYSIS

Run No.	Amount ClO_2	Amount ClO_2 decomposed	Time, min.	Temp., °C.	HClO	HClO ₃	HClO ₄
1	4.82	4.29	45	3	0.34	0.00	0.70
2	14.65	5.87	45	3	1.09	.59	.77
3	21.94	6.62	45	3	1.27	.77	.81

Variation of Decomposition with Time

It can be seen from Table IX that the rate falls off with time. During the first 45 min. period the decomposition is 6.62, during the next period it is 4.83, and during the third it is 3.80.

TABLE IX

Run No.	Amount ClO_2	Amount ClO_2 decomposed	Time, min.	Temp., °C.	HClO	HClO ₃	HClO ₄
1	21.94	6.62	45	3	1.27	0.77	0.81
2	27.36	11.45	90	3	2.25	1.14	1.87
3	22.50	15.25	135	3	2.04	0.88	2.72

NOTE:—Except for time, conditions as above.

Variation of Decomposition with Light Intensity

The change in light intensity was effected by interposing a screen of 36% transmission.

TABLE X
COMPLETE ANALYSIS

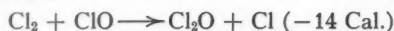
Run No.	Amount ClO_2	Amount ClO_2 decomposed	Time, min.	Rel. I_{abs}	HClO	HClO ₃	HClO ₄
1	27.36	11.45	90	100	2.25	1.14	1.87
2	21.30	4.50	90	36	1.08	0.44	0.72

NOTE:—Light beam as above.

If the decomposition were proportional to I_{abs} , decomposition in Experiment 1 should have been 12.50.

Formation of Chlorine Monoxide

An experiment was performed to determine whether chlorine monoxide is formed by the reaction



Though the reaction is endothermic (about -14 Cal.) reactants with sufficient energy might give chlorine monoxide and chlorine.

Two samples of chlorine dioxide were used; to one, excess chlorine was added. If the reaction above competes with another reaction of the ClO groups (*e.g.*, $\text{ClO} + \text{ClO} \longrightarrow \text{Cl}_2 + \text{O}_2$), increasing the concentration of chlorine should increase the rate of this reaction, and a greater amount of chlorine monoxide should be formed in this case.

TABLE XI
HIGH INTENSITY, COMPLETE ANALYSIS

Run No.	Amount ClO_2	Time, min.	Initial Cl_2	ΔClO_2	Final Cl_2	HClO	$\text{HClO}_2 + \text{HClO}_4$
1	8.96	95	6.25	7.86	12.80	0.58	1.41
2	8.92	95	.94	6.95	5.80	0.53	1.22

This experiment shows that within the accuracy of the analysis there is no difference in the amounts of chlorine monoxide in each run. In Experiment 1 there was greater photolysis. This may account for the slightly greater amounts of ClO^\cdot and $\text{HClO}_2 + \text{HClO}_4$.

Experiments on Stirring

Chlorine dioxide absorbs λ 3650 Å very strongly and, therefore, in the absence of stirring, marked concentration differences are set up during photolysis. It was thus expected that stirring the solutions would alter the rate of decomposition.

TABLE XII

Run No.	Description	Initial ClO_2	Time, min.	ΔClO_2	HClO	HClO_2	HClO_4
1	Unstirred	24.26	30	10.52	1.97	1.29	2.12
2	Stirred	24.06	30	11.60	1.91	1.14	1.94
3	Stirred	15.34	30	11.36	1.13	0.56	2.16

Table XII shows that the photolysis is about 10% greater in a stirred solution. Experiment 3, done with a stirred solution at lower concentration, shows that stirring markedly decreases the effect of concentration on the rate of decomposition. The effect of variation of light intensity may also be negligible in stirred solutions, though this was not tested.

KINETICS OF THE PHOTODECOMPOSITION WITH λ 4360 Å*Effect of Concentration on Rate of Decomposition*

Experiments, similar to those reported above for λ 3650 Å, were carried out with λ 4360 Å. They gave analogous results, *i.e.*, the rate of decomposition in unstirred solutions increases slightly with increasing concentration of chlorine dioxide but decreases with time. They will not be reported further here.

KINETICS OF THE BROMINE SENSITIZED DECOMPOSITION WITH λ 5460 Å*The Influence of Concentration of Chlorine Dioxide*

The results of this study are given in Table XIII. Comparisons are to be made only between values within any series, where the only factor varied is the chlorine dioxide concentration. Concentration of bromine, light intensity, and the period of illumination vary from series to series.

TABLE XIII
DIRECT ANALYSIS

Series	Exp. No.	Initial ClO_2	Per cent absorbed by Br_2	Time, min.	ΔClO_2
1	1	5.71	41	90	0.284
	2	1.71	41	90	.240
2	1	1.22	40	60	.404
	2	2.24	40	60	.389
	3	3.79	40	60	.424
	4	5.35	40	60	.456
	5	8.09	40	60	.396
3	1	12.58	53	60	.532
	2	4.91	53	60	.526
4	1	9.64	71	60	.408
	2	3.71	71	60	.364
	3	1.85	71	60	.440
5	1	0.53	65	45	.438
	2	3.28	65	45	.504
	3	8.35	65	45	.542
6	1	1.26	32	60	.552
	2	3.95	32	60	.632
	3	9.07	32		
7	1	4.65		60	.002
	2	8.48		60	.009

Series 1-4 were done with U.S.P. carbon tetrachloride purified by the method outlined. Series 5-7 were done with c.p. carbon tetrachloride treated in the same way. In Series 7 no bromine was added, so this gives the unsensitized decomposition of the chlorine dioxide by green light. If these values are subtracted (for corresponding concentrations) from those for the sensitized decomposition, there appears to be no significant variation of the decomposition per unit time with chlorine dioxide concentration.

The non-variation of rate of decomposition with chlorine dioxide concentration has also been checked by the procedure for complete analysis.

TABLE XIV

Exp. No.	Initial ClO ₂	Mean ClO ₂	Time, min.	ΔClO ₂	HClO	HClO ₃	HClO ₄
1	9.47	8.08	210	2.77	0.16	0.20	0.54
2	6.25	4.96	210	2.58	-0.01	0.16	0.38

The variation of rate of decomposition with almost twofold change in chlorine dioxide is slight.

Variation of Concentration of Bromine

The results of this study are given in Table XV. Within any series, the only factor varied was the bromine concentration. This quantity is given in terms of the percentage absorption, to which it is related by the expression $\log \frac{I}{I_0} = -\alpha cd$; $\frac{I}{I_0}$ = fraction of light transmitted.

TABLE XV

Series	Exp. No.	Initial conc. ClO ₂	Per cent absorbed	Time, min.	ΔClO ₂	Compare decomp. $\propto I$
1	1	1.57	40.0	60	0.566	1.086
	2	1.57	76.7	60	.952	
2	1	1.74	52.0	75	.450	0.756
	2	1.74	87.3	75	.646	
3	1	1.19	21.7	70	.376	0.908
	2	0.81	52.3	70	.750	

Column 7 gives values calculated from the decomposition with low absorption, on the assumption of a direct proportionality between percentage absorption and rate of decomposition. They are to be compared with the values opposite them in the adjacent column. There is apparently a departure from a linear relation.

Variation of Rate of Decomposition with Light Intensity

The light intensity was varied by interposing screens of the transmission indicated.

It appears that the decomposition does not vary directly as the intensity of the light. In Column 8, Table XVI, values calculated from the decomposition at low intensity are compared, on the assumption of a \sqrt{I} relation. The values calculated on this basis are near, but always below, the values observed.

TABLE XVI

Series	Exp. No.	Initial conc. ClO_2	Relative intensity	Per cent absorption	Time, min.	Decomposition	Compare $\propto \sqrt{I}$
1	1	1.74	36	52.0	90	0.200	0.332
	2	1.74	100	52.0	90	.403	
2	1	1.57	36	65.1	90	.532	.852
	2	1.57	100	65.1	90	.908	
3	1	3.43	36	58.8	60	.228	.380
	2	3.43	100	58.8	60	.428	
4	1	1.13	36	52	70	.394	.658
	2	1.12	100	52	100	.704	
	3	1.13	100		100	.008	
5	1	3.42	51.3	54	60	.466	.552
	2	3.41	100	54	60	.686	
	3	4.58	100		60	.004	
6	1	6.97	100	60	46	1.132	1.00
	2	6.93	36	60	46	0.600	

These results were also checked by doing experiments in which the procedure for complete analysis was used.

TABLE XVII

Series	Exp. No.	Initial ClO_2	Relative intensity	Time, min.	ΔClO_2	Compare $\propto I$	HClO	HClO_3	HClO_4
1	1	2.95	100	180	2.91	4.53	.34	.31	.67
	2	2.98	36	180	1.63		.20	.35	.67
2	1	7.80	36	230	0.82		.30	.23	.37
	2	7.84	100	230	1.96	2.28			

This table also demonstrates that the rate of decomposition does not vary directly as the amount of light absorbed. Greater absorption means relatively less decomposition.

It was considered worthwhile to test whether stirring the solution would alter the rate of decomposition. Parallel runs were made, one solution being stirred, the other being left undisturbed.

It was concluded that stirring makes no difference to the kinetics of the bromine sensitized decomposition.

TABLE XVIII
COMPLETE ANALYSIS, 68% ABSORPTION

Run No.	Description	Initial ClO_2	Time, min.	ΔClO_2
1	Unstirred	5.86	225	1.550
2	Stirred	5.97	225	1.536

Experiments on Bromine Chloride Formation

Papers have appeared in the literature (1, 13, 29) showing that bromine chloride is formed in mixtures of bromine and chlorine in the gas phase and in carbon tetrachloride solution. Since in our experiments chlorine results from the decomposition of chlorine dioxide, it seemed desirable to ascertain whether bromine chloride was formed here.

The amount of bromine chloride formation can be estimated from the change in absorption of the solution for the line 5460 Å. Bromine chloride absorbs this line weakly, whereas bromine shows a strong absorption. ($\alpha_{\text{BrCl}}/\alpha_{\text{Br}} = 0.0405$.) A decrease in absorption should be noticed if bromine chloride is formed.

Some experiments were done with bromine and chlorine mixtures alone in carbon tetrachloride.

Experiment 9N: Br₂ concentration, 2.026; Cl₂ concentration, 2.010. Five minutes after mixing (at room temperature before exposure to light) the free bromine concentration dropped to 1.95, and further change was very slow. On insulating with the full light of the mercury lamp for seven minutes, bromine dropped to 1.025. Further insolation produced no change.

Experiment 10N: Bromine (conc. 2.089) and chlorine (conc. 2.130) were mixed and insulated with green light at 3° C. for two hours. During this time the concentration of bromine dropped to 1.070.

Experiment 11N: The cell contained Cl₂, 2.21; Br₂, 1.3; ClO₂, 1.574. According to a graph experimentally determined, bromine of this concentration should give an absorption of 21.8%; the absorption measured was 22.2%.

Examination of a large number of experiments, of which the above are typical examples, indicates that, whereas bromine chloride is formed in bromine and chlorine mixtures alone, no formation of this compound could be detected under the conditions of these experiments with chlorine dioxide present.

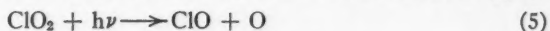
Discussion of Results

Unsensitized Reaction

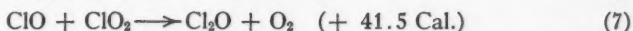
The unsensitized decomposition with λ 3650 Å will be discussed first, since the primary process following light absorption is known. The reaction mechanism must account for (1) the initiation of the thermal decomposition, (2) the formation of Cl₂O, Cl₂O₆, and Cl₂O₇ as well as chlorine and oxygen, (3) the quantum yield of 2, (4) the observed small variation of rate of decomposition with time, concentration of chlorine dioxide and light intensity in unstirred solutions, and non-variation with concentration in stirred solutions.

As stated in the Introduction, absorption of 3650 Å by gaseous chlorine dioxide produces ClO + O. The absorption spectrum of chlorine dioxide in solution appears to resemble in main outline that in the gas phase (16).

Therefore, for the unsensitized reaction at 3650 Å, in solution, we suppose

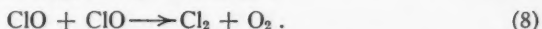


On the assumption that one quantum of light can dissociate one chlorine dioxide molecule, the quantum yield of approximately 2 can be explained by the occurrence of two further reactions:



In the gas phase, a third body is assumed to be necessary to stabilize the collision in Reaction (6). In solution, three-body collisions will be much more numerous, and the reaction may thus be reasonably supposed to take place.

Since only about 10% of the chlorine dioxide decomposed appears as chlorine monoxide, ClO must also disappear by the reaction



This reaction is supposed to have a low activation energy (25) and should thus occur quite readily, probably more readily than Reaction (7).

Actually, if the rate of disappearance of ClO by Reaction (7) is about the same as that by Reaction (8), the expression for the disappearance of chlorine dioxide is:

$$\frac{-d(\text{ClO}_2)}{dt} = k_1 I_{\text{abs.}} + k \sqrt{I_{\text{abs.}}} (\text{ClO}_2)$$

A marked variation with chlorine dioxide concentration and a non-linear variation with light intensity would be expected. Actually, in stirred solutions, the decomposition appears to be independent of chlorine dioxide concentration, and even in unstirred solutions the rate is almost directly proportional to the light intensity.

It is interesting to note that the assumption that Reaction (8) is relatively fast compared to Reaction (7) leads to an expression for the rate of formation of chlorine monoxide.

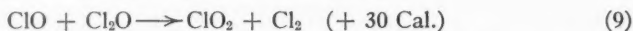
$$\frac{d \text{Cl}_2\text{O}}{dt} = k \sqrt{I_{\text{abs.}}} (\text{ClO}_2)$$

Experiments 1 and 2, Table X, indicate that the formation of chlorine monoxide approaches a \sqrt{I} relation. (In Experiment 1, $\text{HClO} = 3.15$ would have been expected for direct proportionality, $\text{HClO} = 1.80$ for a \sqrt{I} relation.) Reaction (7) provides a mechanism for the formation of chlorine monoxide. The scheme of Luther and Hoffmann (15) can then be used to explain the thermal decomposition initiated by a short insolation at 20° C. The inhibitory effect of water may be attributed to its reaction with chlorine monoxide.

The importance of Reaction (7) is rather difficult to estimate. The value of the molar extinction coefficient for chlorine monoxide at this wave-length, calculated from the value for the gas, is 0.458; that of chlorine dioxide is 1130. Therefore, little decomposition of chlorine monoxide by light absorp-

tion would be expected. Furthermore, experiments have been done which show that chlorine monoxide does not react thermally at an appreciable rate with chlorine dioxide at 3° C.

However, examination of Table IX on the variation of the decomposition with time, shows that at the end of 1½ hr. the chlorine monoxide (represented by hypochlorous acid) is not quite twice that at the end of ¾ hr., and at 2¼ hr. the amount present has fallen off below the value at 1½ hr. To account for this, a reaction of ClO with Cl₂O can be assumed.



Such a reaction will also account in part for the falling-off of the chlorine dioxide decomposition towards the end, since in this reaction chlorine dioxide is built up again. The formation of chlorine dioxide in the photodecomposition of chlorine monoxide makes Reaction (9) quite probable. Chlorine monoxide could also be removed by a chlorine sensitized photodecomposition.

Oxygen atoms combine as is shown by Reaction (6) and also by the reaction



If Reaction (6) is fast relative to Reaction (10), independence of γ from (ClO₂) and light intensity will result.

Cl₂O₆ is formed by polymerization of the ClO₃ groups.



The fact that more Cl₂O₆ is not observed may be due to a number of causes. Cl₂O₆ shows increasingly high absorption towards the blue (11) and decomposes photochemically. Secondary reactions such as



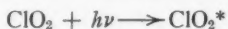
would also tend to prevent the accumulation of Cl₂O₆. The fact that about one-fifth of the chlorine dioxide decomposed goes to the formation of Cl₂O₇ shows that a considerable amount of Cl₂O₆ must have been present.

The reaction with λ 4360 Å appears to be explicable by a similar mechanism.

Since the relative amounts of Cl₂O, Cl₂O₆, and Cl₂O₇ are about the same as with λ 3650 Å, it must be expected that similar groups would be formed in the primary light process.

The wave-length 4360 Å is just at the limit of the region where dissociation to ClO+O is energetically possible. However, a complex molecule in an electronically excited state may be able to make up the required energy in one of the normal vibrations by fluctuations in the energies of the other normal modes of vibration. A molecule of chlorine dioxide absorbing light may thus have a certain probability of dissociating even at a wave-length longer than the limit at which the quantum itself has sufficient energy for dissociation (10). The lower quantum yield can be ascribed to the lower efficiency of the primary light process at this wave-length.

The production of an excited molecule by the process



followed by



will also fit the facts qualitatively. No difference in the relative amounts of products by this process from those at λ 3650 Å would be expected on the basis of the mechanism proposed, and the lower quantum yield could be ascribed to deactivation of the ClO_2^* . However, unless we suppose that a constant fraction of the ClO_2^* reacts with chlorine dioxide, the reaction velocity will depend to a marked extent on (ClO_2) . Thus a splitting into $\text{ClO} + \text{O}$ at 4360 Å is probable.

Sensitized Reaction

We proceed now to a discussion of the bromine sensitized decomposition of chlorine dioxide by λ 5460 Å.

A satisfactory theory should account for the following facts:

- (1) The quantum yield of the decomposition is 0.2 to 0.3.
- (2) The quantum yield does not vary with the chlorine dioxide concentration.
- (3) There is a decrease in quantum yield with increasing light intensity and with increased bromine concentration. The variation of rate of decomposition with light intensity approaches a \sqrt{I} relation.
- (4) Large amounts of Cl_2O_6 and some chlorine monoxide appear to be formed.

In the sensitized decomposition, the light is absorbed by the bromine, and eventually brings about a decomposition of the chlorine dioxide.

The spectrum of bromine in the gas phase shows a convergence limit at 5107 Å. Beyond this there is a continuous absorption region which corresponds to a dissociation of the bromine molecule. The products of the primary dissociation by light absorption in the continuum are one excited and one normal atom. Thus the convergence limit corresponds to the energy that is just sufficient to cause this dissociation. The excitation energy of the excited bromine atom is 0.431 volts. From this the energy corresponding to a dissociation to two normal atoms can be calculated. This energy corresponds to 6250 Å.

The discrete absorption of bromine extends from 6720 Å to the convergence limit. In the region between 6250 Å and the convergence limit, the primary product of light absorption is an excited molecule which has sufficient energy to dissociate to normal atoms if a suitable mechanism is provided; for example, collision with another molecule. There is, however, the possibility that absorption of green light produces bromine atoms directly, since there is a weak continuum underlying the discrete band system.

For bromine in carbon tetrachloride the absorption extends over the same range as for the gas, from 6720 Å to the ultra-violet. The spectrum is continuous throughout the whole region, but the shape of the absorption curve is the same as for the gas (18).

Rabinowitch and Wood have concluded from the behavior of strongly illuminated iodine solutions (19) that iodine dissociates with a quantum yield of 1, even in the discrete region of the spectrum, if the energy of the excited molecule is sufficient for dissociation to two normal atoms.

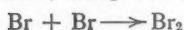
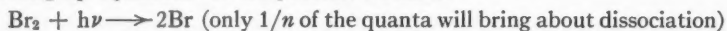
Thus, at the wave-length 5460 Å there is the possibility of the excited bromine dissociating to atoms either directly or on collision with carbon tetrachloride molecules. Wachholtz (30) from a study of the bromine and ethyl maleate reaction, and Schmidt (24) from a study of the bromine and methyl fumurate reaction (both reactions in carbon tetrachloride solution), concluded that the wave-length 5570 Å can produce dissociation to two atoms.

Let us consider the consequences of assuming an atomic process for the bromine sensitized decomposition of chlorine dioxide.

Rabinowitch and Wood (21) have suggested that collisions between particles in solution occur in sets. Two particles once brought together will suffer several consecutive collisions before they are separated. Consider a bromine molecule absorbing a quantum of wave-length 5460 Å. On our assumption, the excited bromine molecule will dissociate when it collides with a solvent molecule. But the two bromine atoms resulting are surrounded by heavy solvent molecules. Before they can separate completely, they may collide again. Since in solution every collision is a three-body collision, this will result in a recombination of the bromine atoms, the solvent molecule and bromine molecule sharing the energy liberated. If, for the conditions existing, n is the average number of consecutive collisions suffered by two inert particles, the probability of the bromine atoms separating before colliding is $1/n$, and therefore the probability of dissociation being fruitful is $1/n$. Thus the average yield of bromine atoms on the absorption of a quantum would be less than 2. The value of the quantum yield would depend on n , and would be $1/n$ of that obtained in the absence of the solvent.

The assumption of bromine atoms bringing about the decomposition of chlorine dioxide would thus explain the low quantum yield of the process; that is, the low yield would be attributed to the high probability of primary recombination.

Setting up equations for the process, we have:



However, it is difficult to provide a mechanism for the reaction products which are observed. The reaction

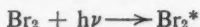


though certainly exothermic (47.2 Cal.), yields no groups which can give rise to Cl_2O_6 or Cl_2O . The reaction



is also unsatisfactory; no reference to bromine oxide has been observed in the literature. An atomic process has therefore to be discarded for want of a plausible mechanism. The other possibility is that absorption of light produces an excited bromine molecule which transfers its energy to a chlorine dioxide molecule by collision.

Hence, the mechanism for the reaction is the same as that proposed for the corresponding gas reaction (27, p. 269).



It appears to be well established that Cl_2O and Cl_2O_6 are formed in this reaction and that the Cl_2O_6 further reacts to give Cl_2O_7 .

To account for these products, the reaction mechanism used to explain the corresponding gas decomposition will serve (Equations (8), (9), and (11) above). The chlorine monoxide then undergoes a bromine sensitized decomposition (22). Cl_2O_7 probably results from the photodecomposition of Cl_2O_6 (either direct or sensitized), but the mechanism of this reaction is not yet known.

To explain the low quantum yield, deactivation of the Br_2^* or of the ClO_2^* might be assumed. Since a solution of bromine in carbon tetrachloride does not fluoresce, there must be deactivation of the excited bromine either by dissociation or by small stepwise energy changes with the solvent molecules.

While the theory outlined above seems to be capable of giving a qualitative explanation of the observations, we have not yet been able to bring it into accord with the independence of the quantum yield from (ClO_2) and its dependence on light intensity. In fact, the latter seems to indicate an atomic mechanism.

The work on the photodecomposition of chlorine dioxide solutions presented in this report is interesting because it shows that there is no great difference between the decomposition (unsensitized and sensitized) in the gas and in solution. The previously supposed difference was very perplexing, because in a number of reactions carbon tetrachloride behaves as an "ideal" solvent. This study adds one more reaction to that list. Apparently the differences that do exist may be attributed to the facts that: (a) in the gas the Cl_2O_6 collects on the walls and is virtually removed from the reaction; in the solution it remains dissolved and undergoes further reaction; (b) in the gas, ClO_3 is always present and may be the carrier for chains; in solution, Cl_2O_6 is the stable form (2).

In addition, this work fits in well with the studies by Luther and Hoffmann on the thermal decomposition. Additional evidence for the existence of chlorine monoxide in insulated chlorine dioxide solutions is presented in the present report.

Further experiments are necessary to clear up the kinetics of the bromine sensitized decomposition. An investigation of the absorption and of the photodecomposition of Cl_2O_6 in carbon tetrachloride solution is needed and is being attempted.

It is hoped that by the comparative study of reactions of relatively simple substances such as chlorine dioxide, progress may be made in the understanding of sensitization and of reactions in solution.

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FORMATION OF OZONE IN AN A-C. LOW PRESSURE DISCHARGE TUBE¹

By M. SENKUS²

Abstract

Passage of a glow discharge through oxygen at a pressure of 25 mm. of mercury and 17,000 volts apparently produces no ozone. The non-production of ozone is due to deoxygenation at the electrodes. A discharge tube is described that can be used for the demonstration and quantitative investigation of the formation of ozone in a glow discharge.

Introduction

The effects of various types of discharges through oxygen at atmospheric pressure have been described in the literature. While studying the effect of a glow discharge through oxygen at pressures of a few centimetres of mercury, some interesting results were obtained which are briefly reported here.

Experimental

Oxygen from a commercial cylinder was passed through a purifying train, and the velocity of the gas measured by a capillary type flowmeter (1). A U-shaped discharge tube (2) was blown from Pyrex glass tubing of 5 mm. inner diameter. Two larger tubes of 12 mm. inner diameter were sealed to the ends of the U-tube. Electrodes of tungsten wire were sealed into two smaller glass tubes which were connected to the 12 mm. tubes by inner seals. The length of the electrodes exposed to the gas was 14 mm. The tips of the electrodes were 15 mm. above the 12 to 5 mm. tubing seals. The inter-electrode distance was 33.5 cm. T-seals, 3.5 cm. above the upper parts of the electrodes, served as outlet and inlet for the oxygen. During all runs this tube was immersed in an ice-water bath to a point above the electrodes.

The ozonized gas from the discharge at pressures between 20 and 50 mm. was analyzed by passing it through a wash flask containing 100 cc. of 3% potassium iodide solution, and thence through a bead tower containing some of the iodide solution. The bead tower was connected through a concentrated sulphuric acid bubbler to a Cenco Hyvac pump. After regulation of the velocity and the pressure of the gas, the voltage was set at a particular value and the gas passed through the discharge for 15 min., after which the residual ozone in the tube was swept out with oxygen. The potassium iodide solution containing the liberated iodine was then acidified with sulphuric acid, and the iodine titrated with a 0.1*N* sodium thiosulphate solution, starch being used as an indicator.

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon. The work was carried out under the direction of the late Dr. A. C. Grubb.

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The source of electrical energy was the 110 volt direct current, alternated by a 60 cycle rotary converter. The alternating current was supplied through a water rheostat to the primary of a Thordarson 25,000 volts, 1 kva, type R transformer. One side of the secondary of the transformer was grounded, while the other was connected to the electrode in the inlet arm of the discharge tube. The secondary circuit was completed by grounding the other electrode. The amperage in the secondary line was measured with a calibrated vacuum tube oscillograph.

Results

Four distinct types of discharge could be obtained with the discharge tube as the potential difference was gradually raised; a non-luminous discharge, a silent discharge, a glow current, and finally a glow discharge (Fig. 1). The type of discharge at a given voltage depends on the pressure.

Only the results obtained with the glow discharge will be described here.

The Glow Discharge

A glow discharge is characterized by a glowing column of gas that extends between the two electrodes. With extremely pure oxygen, the glowing column is greenish; a trace of nitrogen in the oxygen turns it quite yellow. Also, a thick glowing layer of light appears on the electrodes. The extent of surface

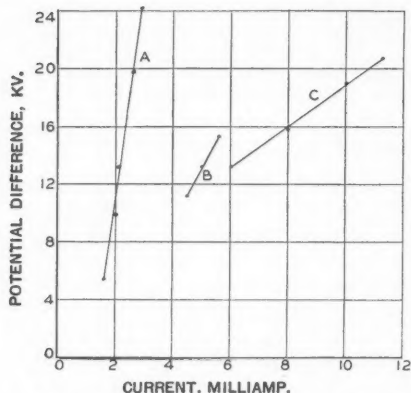


FIG. 1. A, Silent discharge; B, glow current; C, glow Discharge. Pressure, 20 mm.

of the electrodes covered with this glow is roughly proportional to the current passing through the tube.

Ozonization of oxygen in the glow discharge is negligible at atmospheric pressure, apparently owing to thermal deozonization. Determinations of temperatures in the discharge at low pressures showed that far less heat was produced than at atmospheric pressure. The highest temperatures recorded in the tube (when the tube was cooled in an ice-water mixture) was 5° C., except in the immediate vicinity of the electrodes. In air, the gas in the discharge may sometimes attain a temperature of 90° C.

Several attempts were made to estimate the temperature of the electrodes. Closely adhering tin appeared to melt and fall off the electrode at voltages higher than 16,940 volts. Lead continued to adhere. This would indicate that, while the temperature of the electrodes never exceeded 300° C., a temperature of 200° C. was attained.

Ozone Formation in the Glow Discharge

For the tube set up as already described, no ozone was obtained when oxygen was subjected to either the glow current or the glow discharge.

Judging from the conditions obtaining in the tube, it was thought possible that a certain amount of ozone would be formed by the glow discharge, and would be stable in the discharge except in the immediate vicinity of the electrodes. The deozonizing action in this region is due to the high temperature of the electrodes, estimated to be well above 200° C., as well as to the presence of a high concentration of ions. Any ozone formed in the inter-electrode space would therefore be completely destroyed, since all molecules would remain for some time at the surface of, or near, the ground electrode in their passage through the tube.

To ascertain whether any ozonization took place in the inter-electrode space, the gas was pumped off from an exit in the base of the U of the tube. The discharge tube, similar in dimensions to the original one, was constructed of ordinary soft glass. The electrodes were made of platinum. Determinations were made when the gas was pumped off from an exit 4 cm. above the ground electrode, and also from an exit in the base of the U of the tube 15 cm. below the electrode. Results obtained at 25 mm. pressure and a velocity of 1.5 litres per hr. are given in Table I.

TABLE I
OZONIZATION IN THE SILENT AND GLOW DISCHARGES

Exit	Voltage	Type of discharge	Current, milliamp.	Ozone, by weight, %
Top	22,000	Silent	2.63	1.64
Bottom	22,000	Silent	2.63	1.01
Top	16,940	Glow	10.00	0.00
Bottom	16,940	Glow	10.00	0.42

Another discharge tube was constructed for the investigation of the relation between exit to electrode distance and ozone yield. The tube was made by bending a piece of glass tubing 11.8 mm. in inner diameter into a U-shape. A T-seal, 5.5 cm. above the base of the U, served as an exit for the gas. Platinum electrodes were sealed into two smaller glass tubes, which were connected to the 11.8 mm. tubing by paraffined rubber stoppers. The electrodes were thus movable.

TABLE II
EFFECT OF ELECTRODE TO EXIT DISTANCE ON THE
YIELD OF OZONE IN THE GLOW DISCHARGE

Distance from exit to electrode, cm.	Ozone, %	Yield of ozone obtained in 15 min., mg.
10	0.53	0.28
6	0.53	0.28
5	0.46	0.25
4	0.42	0.23
3	0.39	0.21
2	0.35	0.19
1	0.31	0.17
Tip above exit	0.13	0.14
Tip half way down exit	0.07	0.04
Tip below exit	0.00	0.00

NOTE:—Voltage, 15,400; current, 7.2 milliamp.; rate of flow, 1.5 litres per hr.; pressure, 25 mm.

The inter-electrode distance in this study was kept constant at 33 cm. The electrode connected to the high side of the transformer was always above the inlet for the gas. All runs were made at a velocity of 1.5 litres per hr. and at 25 mm. pressure. Initially the ground electrode was 10 cm. above the exit; it was gradually lowered towards and below the exit. The ozone yields at these various points are given in Table II.

Table III shows the effect of pressure on the yield of ozone in the glow discharge. The yield-pressure relation is apparently linear. Elevation of voltage similarly decreases the yield. The results are tabulated in Table IV.

TABLE III
PRESSURE-YIELD RELATION IN THE GLOW DISCHARGE

Pressure, mm. Hg.	22	25	29	32	34
Ozone, %	0.49	0.42	0.33	0.26	0.22

NOTE:—Voltage, 19,800; current, 11.7 milliamp.; rate of flow, 1.5 litres per hr.

TABLE IV
VOLTAGE-YIELD RELATION IN THE GLOW DISCHARGE

Voltage	8,800	9,900	11,000	12,100	13,200	14,300	15,400	16,500	17,600
Ozone, %	0.55	0.54	0.53	0.52	0.52	0.51	0.50	0.48	0.42

NOTE:—Pressure, 25 mm. of mercury; electrode to exit distance, 10 cm.; rate of flow, 1.5 litres per hr.

These experiments demonstrate that appreciable amounts of ozone are formed in a glow discharge in oxygen at low pressures, but that the ozone is completely destroyed by passage over one of the electrodes.

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MICROCHEMICAL TECHNIQUE

II. MODIFICATION OF THE MICROMETHOXYL APPARATUS TO THE VIEBÖCK PROCEDURE¹

BY MORRIS LIEFF², CYRIL MARKS³, AND GEORGE F. WRIGHT⁴

Abstract

A new absorbing chamber, which adapts the methoxyl analysis more conveniently to the Vieböck procedure, is described for the micromethoxyl apparatus. This receiver acts by hindering the gas flow so as to facilitate absorption of methyl iodide.

Although the Vieböck (5, 6) modification of Pregl's micromethoxyl determination method has been adopted by many microanalysts because of its convenience and rapidity, little change (3, 7) has been made in the apparatus. The necessity for making large numbers of methoxyl determinations in connection with the study of lignin in this laboratory has justified the re-design of Pregl's receiver. The latter, although admirably suited to the gravimetric determination of methoxyl, serves no useful purpose in Vieböck's volumetric method. Indeed, because of the slower reaction in the case of the volumetric procedures (4), a single receiver has been found to be insufficient to completely absorb the evolved methyl iodide. The double receiver used in its place is especially inconvenient when a blank on the reagents (which precaution has been found to assure more accurate and reliable results) is carried out in conjunction with the actual analysis (1).

Consequently the Pregl receiver has been replaced by an absorption tube containing four "pockets", in each of which the emerging gas bubble remains until it is displaced by the subsequent bubble. In order to insure that this displacement will always occur, the construction of these pockets requires great care. Their proper depths depend on the size of the ascending bubble, but it is essential that they be only one-half to one-third as wide as long.

This type of receiver can be adapted to the ordinary Pregl apparatus (Fig. 1) by inclining the outlet tube at an angle of about 10° from the vertical. Such a receiver is designed to contain 5 cc. of absorbent up to the bottom of the enlargement bulb, and is efficient enough to render cooling (1, 7) unnecessary. A solution of 10 cc. of 10% glacial acetic acid-potassium acetate (optically pure), containing 1 to 2 drops of bromine, is measured into a 10 cc. graduated cylinder.

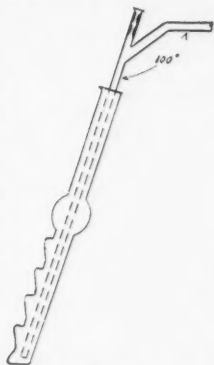


FIG. 1.

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When a mixture of 0.5 cc. of phenol and 2 cc. of hydriodic acid (sp. gr., 1.7) is used to decompose the sample, the apparatus works satisfactorily in a warm room, if reflux is maintained between the two bulbs of the distillation column. The analysis requires a minimum of attention to the all-important rate of gas flow when the generator recommended by Hershberg and Wellwood (2) for the micro-Dumas determination is used as a source of carbon dioxide, since no gas washing is necessary.

Acknowledgment

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XXIX. A STUDY OF THE ACIDIC HYDROXYL GROUPS IN
SPRUCE LIGNIN¹BY R. G. D. MOORE², GEORGE F. WRIGHT³, AND HAROLD HIBBERT⁴

Abstract

A demethylated spruce lignin suitable for further study has been obtained by treating methylated methanol lignin with hydriodic acid. This treatment removes the aliphatic hydroxyl, and leaves 6.9 aromatic and 0.6 carboxylic hydroxyl groups per kg. On the basis of the phenolic content it is estimated that the maximum aromatic content of spruce lignin is about 40 to 45%.

Introduction

Differentiation of the hydroxyl groups in lignin has been complicated by the presence of a multiplicity of types which are difficult to distinguish. Allocation of hydroxyl type is difficult with compounds of low molecular weight because of the non-specificity of reagents used for this purpose, and the difficulties are magnified with a complicated substance such as lignin. In this investigation the problem has been simplified by deliberately destroying the aliphatic hydroxyl groups by a reagent (hydriodic acid) that leaves the aromatic and carboxylic hydroxyl groups unchanged.

Hydriodic acid has previously been employed for reduction of lignins (1, 4, 8), but no attempt has been made to study the reaction product, probably because of its recalcitrant nature. By demethylating a spruce lignin (OCH_3 , 32.4%) (prepared from spruce wood-meal by repeated methylation with dimethyl sulphate and alkali in acetone solution, followed by hydrolysis using the methanol-hydrochloric acid method (2, 3)) by the procedure of Beckmann and co-workers (1), a product was obtained which was soluble enough in organic solvents to permit of a further investigation of its properties. It was also soluble in alkali, and contained 8.3 active hydrogen units per kg. (by the Zerewitinoff analysis in quinoline). After removal of iodine by reduction with zinc and acetic acid the product contained almost no methoxyl or halogen, was soluble in sodium hydroxide, and contained the same number (8.3) of active hydrogen units per kg. (by the Zerewitinoff analysis in quinoline).

When the substance was treated with diazomethane, 7.5 units per kg. of this active hydrogen was methylated (OCH_3 , 21.0%). The remainder (8.3 - 7.5) is probably the aliphatic hydroxyl group formed by reduction, with zinc and acetic acid, of the lignin carbonyl group (0.8 group per kg.) present in spruce lignin (9). These Zerewitinoff analyses were confirmed by

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(a) tosylation, and (b) dimethyl sulphate methylation, the latter carried out under such pH conditions that the carbomethoxyl linkages were not hydrolyzed. The methoxyl value (23.0%) accounts for all of the 8.3 active hydrogen units found in the demethylated product.

When the demethylated product is tosylated, both aliphatic and aromatic hydroxyls are replaced. Since the tosyl content is only 7.7 groups per kg., the balance, 0.6 group ($8.3 - 7.7$) corresponds to the residual active hydrogen content (0.8 unit per kg., Zerewitinoff analysis in quinoline), and shows that 0.5 to 0.8 hydroxyl group is present which is neither aliphatic nor aromatic. That this is carboxylic is shown by saponifying the diazo-methane-methylated substance (OCH_3 , 21.0%), whereby the methoxyl is decreased to 19.2% (ca. 0.6 group per kg.)

By subtracting this carboxyl content of 0.6 group per kg. from the total acidic hydroxyl content (7.5 per kg.) there remain 6.9 groups per kg. which must be aromatic hydroxyl, since aliphatic enolic linkages presumably would not have survived the reduction with hydriodic acid. According to Fuchs (5), alkali fusion of spruce lignin yields 5.5 parts of protocatechuic acid to one part of *p*-hydroxybenzoic acid. Application of this ratio to the 6.9 aromatic hydroxyl groups per kilogram of demethylated lignin would require about 2.9 pyrocatechol and 1.1 phenol nuclei per kg. or a maximum of about 40 to 45% of aromatic nuclei in spruce lignin.

The actual aromatic material isolated unchanged from spruce lignin has been found to contain the guaiacyl radical (6, 7). On the assumption that all the methoxyl groups are thus attached to the aromatic portion (40%), the methoxyl content of isolated lignin should be less than 12%. Most isolated spruce lignins contain 13 to 17.5% OCH_3 ; it is therefore probable that part of the methoxyl content in isolated lignin is non-aromatic in character.

Experimental

The methylated spruce lignin used (2, 3) contained: OCH_3 , 32.4; C, 66.4; H, 6.6%.

Demethylation

A solution of 10 gm. of this lignin in 800 cc. of glacial acetic acid and 100 cc. of hydriodic acid (sp. gr. 1.7) was boiled for two hours while carbon dioxide was bubbled through the solution.

Fractionation

The solution was then concentrated to 200 cc. (18 mm.), the residue poured into dilute sodium bisulphite solution (3 litres), and the precipitate (5.5 to 6.0 gm.) removed by centrifuging. The liquors were concentrated (20 mm.) and then extracted with ether; this yielded 2.5 gm. of tarry residue, not identified. The lignin-like precipitate was dissolved in dioxane and reprecipitated by pouring the dioxane solution into 10 volumes of ether. Yield, 0.9 gm. Found: C, 63.2; H, 5.0; OCH_3 , 0.7; I, 5.9%. The precipitating liquors were concentrated and poured into 10 volumes of petroleum ether

(b.p. 30° to 50° C.*). Yield of precipitate, 4.2 gm. Found: C, 63.5; H, 5.7; OCH₃, 0.7; I, 8.2%. Only methyl iodide (isolated as methyl pyridinium iodide) was found in the effluent gases.

De-iodination

The unfractionated, demethylated product was refluxed for one hour with approximately 150 times its weight of glacial acetic acid and five times its weight of zinc dust. The solution was cooled, filtered, concentrated to a small volume under reduced pressure, and the lignin precipitated by pouring into 10 volumes of water. Fractionation by the procedure outlined above yielded a dioxane-ether insoluble lignin (15%, Fraction A) and a dioxane-petroleum ether (30° to 50° C.) insoluble lignin (80%, Fraction B). Found: (A) C, 68.2; H, 5.4%; I, none. (B) C, 60.0; H, 7.0%; active hydrogen in quinoline, 8.3 per kg.

Diazomethane Methylation

Dioxane solutions of the de-iodinated products (A) and (B) were treated four times with gaseous diazomethane. Reaction product after purification showed: (A) OCH₃, 20.0%; (B) OCH₃, 21.0%. When (B) was boiled for nine hours with 5% ethyl alcoholic potassium hydroxide the methoxyl was decreased to 19.2%.

Dimethyl Sulphate Methylation

A sample (0.3 gm.) of diazomethane-methylated product (B) was acetylated for three days with pyridine (5 cc.) and acetic anhydride (2 cc.). The acetylated material was treated immediately in acetone solution (20° C.) with dimethyl sulphate (6 cc., 0.06 mole) and 30% sodium hydroxide (7 cc., 0.05 mole). After a similar re-methylation the product, dissolved in dioxane solution, was precipitated by pouring the solution into 10 volumes of petroleum ether (b.p. 30° to 50° C.); OCH₃, 23.0%.

Tosylation

It was found that the aliphatic hydroxyl group which could be methylated with dimethyl sulphate (acid conditions), but not with diazomethane, could be tosylated when 6.2 gm. of the diazomethane-methylated product (OCH₃, 21.0%) was treated in 10 cc. of pyridine with one gram of tosyl chloride for 100 hr. at 20° C. After precipitation by pouring into potassium bicarbonate solution the product was filtered off, washed with water, dried, and re-precipitated from dioxane solution by pouring into 10 volumes of petroleum ether (30° to 50° C.); OCH₃, 16.3; S, 2.9%.

When 1.5 gm. of the de-iodinated product (B) was tosylated twice in 55 cc. of pyridine with 6 gm. of tosyl chloride as outlined above, the product contained 11.3% sulphur (no nitrogen or halogen) and 0.8 active hydrogen per kg. (in quinoline). Calcd. for 7.7 tosyl groups per kg.: S, 11.3%.

* Skellysolve F.

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THE DELIGNIFICATION OF WOOD BY STRONG ALKALINE SOLUTIONS¹

BY G. R. LUSBY² AND O. MAASS³

Abstract

The delignification of wood by means of sodium, potassium, and lithium hydroxides has been determined with alkaline concentrations from 1.4 to 14.3 molar, and at temperatures from 120° to 180° C. A small-scale experimental technique was used by means of which the time, temperature, and concentration variables could be closely controlled.

It was found that delignification increased with concentration. A 2.9 *M* solution reacted about twice as fast as a 1.4 *M* solution of sodium hydroxide at 160° C. The difference in rate of reaction is less for solutions of concentrations of 2.9 and 4.5 *M*. Potassium hydroxide of 1.4 *M* concentration reacts only slightly more readily than sodium hydroxide of the same concentration, but the difference in reaction rate becomes more marked with increase in concentration. Lithium hydroxide reacts much more slowly than either of the other two hydroxides. There is a marked increase in reaction rate with increase in temperature. A ten degree rise in temperature somewhat more than doubles the rate of delignification. The rate of reaction is considerably diminished by the presence of sodium chloride or of reaction products in the cooking liquor.

Introduction

When wood is cooked with alkali, for the manufacture of paper-pulp, the non-cellulosic substances go into solution very rapidly at high temperatures, with the exception of the lignin, which is dissolved comparatively slowly. Because of this fact, the cooking process has been regarded in this research as the separation of lignin from cellulose. The dissolving of other wood substances is considered as incidental to the removal of lignin; that is, the main reaction is between lignin and alkali.

A preliminary study of this problem was made by Macklin and Maas (3), who investigated the rate of delignification of spruce wood by sodium hydroxide at 160° C. over the concentration range 6.2 to 14.3 molar. Their apparatus was used in the present investigation, and the technique was also the same except for a few minor changes. Studies of other problems related to the general investigation of the mechanism of alkali-cooking have been made by Richardson and Maass (4), who have measured the sorption of sodium hydroxide on cellulose; by Lusby and Maass (2), who studied the natural penetration of electrolytes into wood; and by Larocque and Maass (1), who examined the effect of the forced penetration of the liquor upon the alkaline delignification of wood.

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² Holder of a scholarship from the Pulp and Paper Association at the time of the investigation. At present, Research Chemist, Canadian Industries Limited.

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In the present investigation, a study has been made of the influence upon the rate of delignification of (1) concentration, (2) different alkalis, (3) temperature change, and (4) neutral salts and reaction products in the cooking liquor.

Apparatus and Experimental Procedure

The apparatus and method of operation, and the analytical methods used were the same as those described by Macklin and Maass (3) in their preliminary investigation of the alkaline delignification of wood. Briefly, the experimental method consisted in cooking a 10 gm. sample of chips of black spruce wood in a small 80 cc. capacity allegheny metal digester, which was immersed in a pail of hot oil maintained at 160° C. or any other desired temperature by means of a thermoregulator.

A continuous flow of fresh liquor from a reservoir passed through the cell throughout an experiment. The rate of flow was sufficiently great that the concentration of the outgoing liquor was practically identical with the concentration of the incoming liquor. A constant pressure of about seven atmospheres was maintained inside the cell by means of a cylinder of compressed nitrogen connected through a reducing valve. At the end of an experiment the flow of liquor was stopped and the pail of oil replaced by a pail of cold water. When the cell had cooled the latter was removed, the liquor blown out of the cell by means of the nitrogen, and the cell dismantled. This experimental procedure gave an accurate control over each of the main factors governing the reaction, viz., temperature, concentration of alkali, and time.

The cooked chips were removed from the cell at the end of the experiment, placed in a dilute solution of hydrochloric acid, and disintegrated into single fibres by means of a high speed stirrer. The pulp was then washed on a Büchner funnel with water. The washed pulp was dried at 105° C. to obtain the yield of "original pulp". Duplicate samples of the pulp were then analyzed for lignin by the Ross-Potter method (5). Duplicate samples of the pulp were extracted with 1% sodium hydroxide to remove any alkali soluble lignin. The extracted pulp was then analyzed for lignin. All results were expressed as a percentage of the original bone-dry weight of the wood.

The different samples of wood used contained from 29 to 32% of lignin. In the calculation and plotting of the extent of delignification, a value of 29% was used for the lignin content of the wood, which made the results comparable with those of Macklin and Maass (3).

The sodium hydroxide used in most of the experiments was a technical grade (analysis: NaOH, 95; Na₂CO₃, 3.5; NaCl, 1.5%—on a dry basis). A 1 : 1 solution was made up and allowed to stand until the sludge settled. The clear solution was then decanted off and diluted to the desired concentration. This procedure gave a solution practically free from carbonate. No appreciable difference was noticed between the results obtained with "technical" and c.p. grades of sodium hydroxide. The potassium hydroxide was of U.S.P. quality containing 85% KOH, the impurities being carbonate and water. The lithium hydroxide was of "Merck" quality.

Experimental Results

1. Preliminary Experiments

Some preliminary runs in which the rate of flow of the liquor was varied indicated that diminishing the rate of liquor flow resulted in a decreased amount of changed lignin being able to diffuse outward from the chip, the extent of the delignification remaining practically the same. These results were confirmed in other runs in which it was found that wood samples cut into thin sections contained less changed lignin than thicker specimens cooked under otherwise identical conditions. Again, the same amount of delignification took place, but apparently in the thinner sections of wood the rate of diffusion of the changed or alkali-lignin was increased owing to the shorter distance that the micelles of alkali-lignin had to travel to enter the liquor. Some general conclusions may be made as a result of these and other confirmatory experiments.

(1) Variations in the volume of liquor sent through the digester cell, and small variations in the lignin content of the wood and in the wood density seemed to have no noticeable effect on the extent of the delignification, within the limits of the experimental accuracy.

(2) The chip thickness and the volume of liquor sent through the digester cell appeared to influence, by their effect on the concentration gradient of lignin in solution inside and outside the chip, the amount of changed lignin entering the liquor.

(3) The same delignification is obtained with wood of the regular chip size used in this work and with wood in very thin sections. This was expected from the rapid rate of diffusion observed by Lusby and Maass (2) on the natural penetration of sodium hydroxide into wood.

2. The Influence of Concentration on Rate of Delignification

The delignification data given in Table I are plotted on a time basis in Fig. 1. Concentration is seen to play an important part in the rate of reaction between sodium hydroxide and lignin. An examination of the figure indicates that a 2.9 *M* sodium hydroxide solution reacts with lignin about twice as fast as a 1.4 *M* solution. The difference in rates of reaction is not as great between 2.9 and 4.5 *M* sodium hydroxide. The delignification values at the end of one hour for concentrations greater than 4.5 *M* are somewhat higher than those found by Macklin and Maass (3). The difference may be due to the use of a different sample of wood.

3. Cooking with Potassium and Lithium Hydroxides

(a) Effect of Concentration

In Table II are given the data obtained in a series of cooks with potassium hydroxide and lithium hydroxide. The data obtained in one-hour cooks are plotted in Fig. 2. It would appear that at the lower concentrations potassium hydroxide and sodium hydroxide react with lignin at nearly the same rate;

TABLE I
DELIGNIFICATION WITH SODIUM HYDROXIDE

Run No.	Alkali concentration, <i>M</i>	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignification, %
8	1.4	0.5	66.3	21.5	7.5
9	1.4	1.0	57.9	15.5	13.5
5	1.4	1.5	54.4	12.4	16.6
10	1.4	2.0	50.2	8.7	20.3
1	1.4	3.0	44.6	5.6	23.4
11	2.9	0.5	61.8	17.1	11.9
12	2.9	1.0	51.4	10.4	18.6
13	2.9	1.0	53.9	8.7	20.3
14	2.9	1.5	46.8	6.1	22.9
15	2.9	2.0	40.5	3.0	26.0
16	2.9	3.0	35.0	2.3	26.7
17	4.5	0.5	66.0	16.3	12.7
71	4.5	1.0	49.9	7.9	21.1
18	4.5	1.25	44.7	5.3	23.7
19	4.5	2.0	34.6	1.6	27.4
20	4.5	3.0	28.7	0.5	28.5
66	6.1	1.0	46.9	7.3	21.7
69	6.3	1.0	44.9	6.4	22.6
67	8.1	1.0	44.4	5.4	23.6
70	8.1	1.0	44.5	5.3	23.7
72	8.1	3.0	28.5	1.5	27.5
73	9.7	3.0	29.5	0.8	28.2

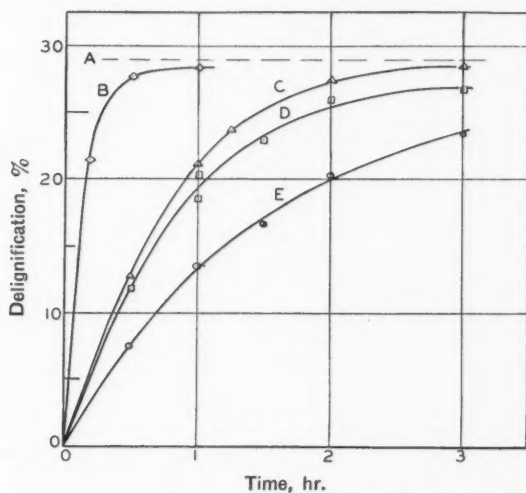


FIG. 1. Delignification at 60° C. A, total delignification. B, potassium hydroxide, 14.3 *M*. C, D, and E, sodium hydroxide. C, 4.5 *M*; D, 2.9 *M*; E, 1.4 *M*.

but as the concentration is increased, the difference in behavior of these two hydroxides becomes more noticeable. It is evident from the figure that lithium hydroxide reacts much more slowly.

TABLE II
DELIGNIFICATION WITH POTASSIUM AND LITHIUM HYDROXIDES

Run No.	Concentration, <i>M</i>	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignification, %
<i>Potassium hydroxide</i>					
21	1.39	1.0	60.3	15.0	14.0
22	2.90	1.5	46.5	4.6	24.4
23	2.88	1.0	50.9	8.3	20.7
24	4.56	0.5	58.5	10.1	18.9
25	4.53	1.0	44.7	4.8	24.2
26	6.26	1.0	47.4	3.4	25.6
27	9.6	1.0	46.6	1.6	27.4
31	14.3	0.17	53.1	7.5	21.5
32	14.3	0.50	43.9	1.2	27.8
28	14.2	1.0	42.1	0.6	28.4
<i>Lithium hydroxide</i>					
29	1.38	1.0	59.4	17.2	11.8
30	2.89	1.0	62.7	15.4	13.6

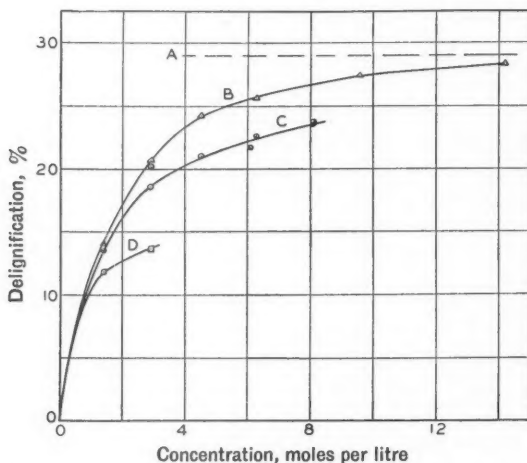


FIG. 2. Delignification in one-hour cooks with sodium, potassium, and lithium hydroxides. Temperature, 160° C. A, total delignification. B, potassium hydroxide; C, sodium hydroxide; D, lithium hydroxide.

(b) Effect of Time on Delignification

The shape of the delignification-time curve for the 14.3 *M* potassium hydroxide is shown in Fig. 1. For the 10 min. run the chips were cut into thin sections similar to planings, to permit as rapid penetration as possible of the liquor into the wood. This is an important consideration when the cooking time is only 10 min.

4. Effect of Temperature on Delignification Rate

Runs were made with sodium and potassium hydroxides of different concentrations at 120°, 140°, and 180° C. The data obtained are given in Table III. It is to be observed that there is a marked increase in the delignification with rise in temperature, the rate approximately doubling with a 10 degree rise in temperature. The significance of these results will be fully discussed in a subsequent paper.

TABLE III
THE INFLUENCE OF TEMPERATURE

Run No.	Con- centration, <i>M</i>	Temp., ° C.	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignifi- cation, %
<i>Reagent—Sodium hydroxide</i>						
33	2.9	140	1.0	66.5	23.2	5.8
34	2.9	180	1.0	17.0	0.4	28.6
35	14.3	120	1.0	78.2	24.1	4.9
36	14.3	140	1.0	59.1	11.7	17.3
37	14.3	140	3.0	36.4	1.2	27.8
<i>Reagent—Potassium hydroxide</i>						
38	14.3	120	1.0	70.3	23.6	5.4
39	14.3	140	1.0	52.6	4.6	24.4

5. The Influence of Sodium Chloride in the Cooking Liquor on the Rate of Delignification

The effect of added sodium chloride in the cooking liquor on the rate of delignification can be seen in Table IV. The cooking liquor was made up by adding a definite amount of sodium chloride to 2.9 *M* sodium hydroxide.

TABLE IV
THE INFLUENCE OF SODIUM CHLORIDE ON THE RATE OF DELIGNIFICATION

Run No.	Reagent	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignifi- cation, %
42	{ 2.97 <i>M</i> NaOH 4.26 <i>M</i> NaCl }	1.5	61.1	12.9	16.1
43	{ 2.97 <i>M</i> NaOH 4.26 <i>M</i> NaCl }	3.0	47.1	6.4	22.6
14	2.90 <i>M</i> NaOH	1.5	46.8	6.1	22.9
16	2.90 <i>M</i> NaOH	3.0	35.0	2.3	26.7

Since the increase in volume accompanying the dissolving of this salt decreased the molar concentration of the alkali, the final concentration was adjusted to give the same molar concentration of sodium hydroxide as the liquor to which no sodium hydroxide was added.

The addition of 4.26 moles of sodium chloride to a 2.9 *M* solution of sodium hydroxide decreases the rate of reaction to about one-half its value when this salt is absent. This decreased activity of the sodium hydroxide in the presence of the chloride is to be ascribed to a common-ion effect taking place; this depresses to some extent the dissociation of the sodium hydroxide.

6. The Influence of Reaction Products on the Rate of Reaction

Some experiments were carried out in order to study the influence of the reaction products on the rate of the delignification reaction. The results obtained are set forth in Table V, along with the mean of two control experiments.

TABLE V

THE INFLUENCE OF THE REACTION PRODUCTS ON THE RATE OF DELIGNIFICATION AND OF MERCERIZATION IN STRONG ALKALI

Run No.	Reagent	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignification, %
12, 13	2.90 <i>M</i> NaOH	1.0	52.7	9.6	19.4
46	2.90 <i>M</i> NaOH ¹	1.0	61.3	15.6	13.4
47	2.90 <i>M</i> NaOH ²	1.0	56.0	13.3	15.7
48	2.90 <i>M</i> NaOH ³	1.0	60.1	14.2	14.8
50	2.90 <i>M</i> NaOH ⁴	1.0	50.4	9.1	19.9

NOTE.—¹ 52 gm. per litre of redissolved alkali-lignin added.

² Waste-liquor containing 38 gm. per litre alkali-lignin.

³ 100 gm. per litre of cellulose decomposition products.

⁴ Mercerized for eight hours in 14 *M* NaOH.

In the first experiment, Run 46, the cooking liquor contained 52 gm. per litre of redissolved alkali-lignin, prepared by triturating the required amount of dry alkali-lignin in a mortar with 2.90 *M* sodium hydroxide solution. Sufficient fresh alkali was then added to this solution to restore the concentration to the original value of 2.90 *M*. It was realized that in this first experiment, the redissolved alkali-lignin might not have the same action as alkali-lignin which goes into solution during the cooking process. In a second experiment, Run 47, a waste liquor freshly obtained from a previous soda-cook was used, containing 38 gm. per litre of alkali-lignin, and of 2.90 *M* concentration with respect to sodium hydroxide, as determined by titration.

In a third experiment, Run 48, the liquor contained 100 gm. per litre of cellulose decomposition products. These decomposition products were obtained by heating 200 gm. of bleached soda-pulp at 180° C. for one hour in 1800 cc. of 2.90 *M* sodium hydroxide. At the end of this time, 85% of

the soda-pulp had dissolved to give a dark reddish-brown liquor. The alkalinity of this liquor was built up to 2.90 *M* and the liquor used in the cooking experiments reported in Table V.

A consideration of the results of this table indicates that the presence either of alkali-lignin, or of cellulose decomposition products in the cooking liquor, markedly decreases the rate of reaction. It is to be noticed that the presence of the alkali-lignin seems to have a more pronounced effect than the same amount of cellulose decomposition products. Both the alkali-lignin and the cellulose decomposition products are known to exist in the liquor as colloids, which absorb alkali. It is therefore likely that this decrease in the rate of delignification is due to a decrease in the effective alkali concentration due to the loss of sodium hydroxide by sorption by these colloids. This lower effective concentration of alkali would not be apparent on titration, because the adsorbed alkali would return to the solution as neutralization took place.

7. The Influence of Swelling on the Rate of Reaction

It was thought that the increased rate of reaction that is observed at the higher alkali concentrations might in part be due to a change taking place in the molecular arrangement of the lignin particles, brought about at the same time as the swelling of the cellulose which occurs as the result of the sorption of alkali at high concentrations of sodium hydroxide. In one experiment (Run 50, Table V), wood chips were allowed to stand for eight hours at room temperature in absorption equilibrium with 14 *M* alkali, after which most of the alkali was removed with water. Subsequent cooking with 2.90 *M* alkali gave the same residual lignin content as the control experiment. This indicates that pretreatment involving swelling of the cellulose has no influence on the rate of subsequent delignification. The increased activity at higher alkali concentrations would seem to be a specific property of the more concentrated solutions.

Discussion

The results of the experiments with 1.4, 2.9, and 4.5 *M* sodium hydroxide solutions are not directly comparable with the results that would be obtained with liquors of the same composition under commercial conditions, since it has been shown that the presence of reaction products considerably slows up the cooking reaction. They may be compared in a relative way, however, and give an accurate indication of the influence that concentration plays in the alkaline-delignification reaction. In commercial pulping practice, it has been commonly observed that the addition of "black liquor" to the cooking liquor increases the bleach requirement of the pulp. It may be that the increased quantity of reaction products in the liquor caused this effect by decreasing the extent of the cooking.

Ross (5) found that pulp of commercial quality could be made by cooking wood with 14 *M* sodium hydroxide solution, and the same should be true of cooking with 14 *M* potassium hydroxide solutions. The much greater rapidity

of cooking which obtains in the case of potassium hydroxide would depend upon the efficiency of the recovery system and the desirability of the pulp in regard to its physical and chemical properties.

From the investigation of the rates of reaction of lithium, sodium, and potassium hydroxides with lignin in wood, the generalization may be made that the rate of reaction increases with the atomic weight of the alkali metal. Rubidium and caesium hydroxides would be expected to react with lignin even faster than does potassium hydroxide. In a subsequent paper an attempt will be made towards elucidating the mechanism of the lignin-alkali reaction, by comparing the rates of reaction obtained with different alkalis with data on viscosity, activity, absorption, etc., of the alkali solutions employed.

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